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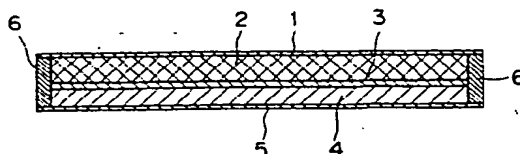
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(54) **BATTERY.**

(57) A battery composed of a composite positive plate (2), a composite negative plate or a negative plate (4), an electrolyte layer (3) and a sealing member (6). The battery uses a substance, such as palladium, belonging to the Group VIII of the Periodic Table. A gas generated inside the battery is adsorbed on such a substance and is added to a remaining reactive double bond in an ion-conductive polymer. Accordingly, the rise of the internal pressure due to the gas can be restricted, and expansion and breakage of the battery can be prevented.

Fig.1



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Technical Field

This invention relates to a battery operating reversibly under an environmental temperature, electrodes and an electrolyte of which are improved.

Background Art

With a recent tendency to design various electric equipments into micro-electronic forms, a demand for a battery has been increasing, which is small in size, light in weight and thin in thickness, and provided with a high energy density. In a field of primary battery, a small-sized and light-weight battery such as a lithium battery has already been put to practical use. However, its application field has been limited to a small region. In a field of secondary battery, a battery utilizing non-aqueous electrolyte, which can be made smaller in size and weight, attracts public attention at present as an alternate battery in place of a conventional lead-battery and a nickel-cadmium battery.

Here, in order to obtain a small-sized and light-weight battery having a high energy density and a high reliability, it is necessary to examine the following problems (1) and (2).

(1) Problem of electrode active material and electrode

(2) Problem of electrolyte

Electrode active materials utilizing intercalation and doping phenomena of layer compound are specially studied now in many research organizations. These materials are expected for their extremely excellent charge/discharge cycle characteristics, because a theoretically complicated chemical reaction does not take place at time of electrochemical reaction in charging and discharging. However, in such electrode active materials, expansion and contraction of the electrode active material are produced accompanied by charging and discharging. To cope with this problem, it is required to improve mechanical strengths of the electrode and electrolyte.

A liquid electrolyte, especially prepared by dissolving ionic compound in an organic electrolyte, has so far been generally used for an electrolyte. However, since there have been troubles such as easiness of leakage of electrolyte to battery outside and easiness of elusion and evaporation of electrode material etc. when the liquid electrolyte has been used, problems of inferiority in long-term reliability and flying-around of electrolyte in a sealing process have remained unsolved. As a means to solve these problems, that is, a means to improve a solution-leakage resistance and a long-term reliability, an ion-conductive high-molecular compound having a high ionic conductivity has been reported and further studied.

When the ion-conductive high-molecular compound is used as an electrolyte for electrochemical device, it becomes necessary to make the electrolyte into a film shape in order to reduce an internal resistance. Especially, this is important for a film type battery. In case of the ion-conductive high-molecular compound, it is possible to work its uniform film easily into a voluntary shape, and various methods for this purpose are known. Heating and polymerizing method has so far been used frequently because of its conveniency. However, the heating and polymerizing method has included the following problems.

(1) It is hard to increase a manufacturing speed because a heating and polymerizing time becomes very long.

(2) It is hard to carry out uniform polymerization because a temperature gradient is apt to be produced in a heating furnace.

(3) The heating furnace and its auxiliary facility become large because the heating must be done in an atmosphere of inert gas.

(4) A cross-link network structure becomes more irregular because displacement of polymerization initiator occurs in composition liquid of the ion-conductive high-molecular compound.

Incidentally, following serious problems were brought about when using the ion-conductive high-molecular compound for the battery. As the charge/discharge cycles were repeated; water content was extracted from a cathode composite, this water content reached an anode through an electrolyte layer comprising the ion-conductive high-molecular compound, the water content reacted with a lithium metal of the anode to produce hydrogen gas, and a battery inside pressure was increased by this hydrogen gas. As a result, troubles such as expansion and bursting of battery took place to impair a long-term reliability and safety.

This invention is made in consideration of the above present circumstances, and an object of it is to provide a battery which can prevent expansion and bursting to improve the long-term reliability and safety, can improve a charge/discharge cycle characteristic, and further can make a workability better.

Disclosure of the Invention

A battery of this invention is characterized by that it is equipped, in an inside surrounded by a current collector and a sealing material, with a cathode composite including an active material and a material other than it, an anode composite including an active material and a material other than it or an anode comprising the active material only, and an electrolyte; an ion-conductive high-molecular compound including one or more kinds of ionic compound in a dissolved state is used as a composition material, for at least one of the cathode composite, the anode composite and the electrolyte; one or more kinds of materials having such property that gas produced in a battery inside is absorbed by the material itself or added to residual reactive double bond in the ion-conductive high-molecular compound, are included in the battery inside.

In this invention, the gas produced in the battery inside is absorbed by the material or added by the material to the residual reactive double bond in the ion-conductive high-molecular compound, so that an increase in a battery inside pressure due to gas is restrained and the expansion and bursting of battery are thus prevented. The ion-conductive high-molecular compound is formed by polymerization of a specified high-molecular compound. However, it is confirmed that the reactive double bond remains by about 5% max. even when the compound is polymerized by irradiation of ionizing radiation or ultraviolet ray.

In case when the electrolyte layer is composed of the ion-conductive high-molecular compound, a formation of dendrite when using lithium for the anode is restrained and a liquid-leakage resistance i.e. a long-term reliability can be improved. Further, since a mechanical strength of the electrolyte layer is made better, a short-circuiting at times of manufacture of battery and charge/discharge cycle can be prevented.

The above-mentioned materials may exist anywhere in the battery inside. For example, (1) Inside or surface of the cathode composite, (2) Inside or surface of the anode composite, (3) Surface of the anode, (4) Surface of the sealing material, and (5) Inside of electrolyte layer etc. may be mentioned.

For the foregoing materials; elements belonging to VIII-group in periodic table such as palladium, ruthenium, rhodium or platinum etc. may be used. Further, palladium-treated carbon, palladium-treated MnO_2 , platinum black, platinum-treated carbon, misch metal alloy or LaNi_5 may be used. As the misch metal alloy, $\text{MmNi}_{3.7}\text{Fe}_{0.3}\text{Al}_{0.3}\text{Co}_{0.7}$ may be mentioned. These materials offer good absorbing property to hydrogen gas. Elements belonging to III-group or V-group are specially excellent for the metal which absorbs hydrogen gas. Further, active carbon zeolite, hollow glass fine sphere, ethyl ether, acetone, gelatin, starch or dextrin may be used too, although they are inferior in the absorbing property. A binder may be included in at least one of the cathode composite and the anode composite. By including these materials, the mechanical strength of electrode can be improved. The expansion and contraction of electrode accompanied by repeated charging/discharging can be eliminated so that the charge/discharge cycle characteristic can be improved from this point too.

A binder is prepared by dissolving or dispersing an organic compound, which will be described later, in a solvent such as dimethylformamide or xylene etc., for example. As the organic compound, polymer or copolymer of the following compounds may be mentioned. As the compounds; acrylonitrile, methacrylonitrile, vinylidene fluoride, vinyl fluoride, chloroprene, vinylpyridine and their derivatives, vinylidene chloride, ethylene, propylene, straight-chain diene, cyclic diene etc., may be mentioned. As the cyclic diene; cyclopentadiene, 1,3-cyclohexadiene etc., for example, may be mentioned.

As methods for including the binder into the electrode; a method in which the foregoing organic compound is dissolved in solvent, the active material and the ion-conductive high-molecular compound etc. are dispersed in it, and the prepared solution is used as a coating liquid; and a method in which the active material and the ion-conductive high-molecular compound etc. are dispersed in a dispersant comprising the foregoing organic compound and a dispersant for dispersing the compound, and the prepared solution is used as a coating liquid etc., are generally used.

It is desirable to form the ion-conductive high-molecular compound by polymerization reaction produced by irradiation of ionizing radiation or ultraviolet ray. According to this method, a workability is improved as compared with the case of the heating and polymerization method.

As the ionizing radiation; γ -ray, X-ray, electron beam and neutron beam etc. may be mentioned. The method using these ionizing radiations works very efficiently when the above-mentioned ion-conductive high-molecular compound is cross-linked. Namely, a degree of cross-linking of the ion-conductive high-molecular compound can be controlled easily by controlling an amount of irradiation and various electrodes and electrolytes, which are optimum from electrochemical standpoint, can be made up. In addition, the ionizing radiation is excellent in an energy efficiency, too.

As the foregoing ion-conductive high-molecular compound; a compound may be mentioned which is prepared by polymerizing a high-molecular compound having reactive double bond and polyether bond so as to have a crosslink network structure. For example, a compound prepared by polymerizing monoacrylate

or monomethacrylate of polyethylene glycol with diacrylate or dimethacrylate of polyethylene glycol may be mentioned. Since such the ion-conductive high-molecular compound is a crosslink polymer formed by ether bond, it does not include intermolecular hydrogen bond so that its structure has a low glass transition temperature. For this reason, migration of dissolved ionic compound becomes extremely easy in such the ion-conductive high-molecular compound.

As the ionic compound; inorganic ionic salts including one kind of Li, Na or K such as LiClO_4 , LiBF_4 , LiAsF_6 , LiPF_6 , LiI , LiBr , $\text{Li}_2\text{B}_{10}\text{Cl}_{10}$, LiCF_3SO_3 , LiCF_3CO_2 , LiSCN , NaI , NaSCN , NaBr , NaClO_4 , KClO_4 and KSCN etc.; quaternary ammonium salts such as $(\text{CH}_3)_4\text{NBF}_4$, $(\text{CH}_3)_4\text{NBr}$, $(\text{C}_2\text{H}_5)_4\text{NClO}_4$, $(\text{C}_2\text{H}_5)_4\text{NI}$, $(\text{C}_3\text{H}_7)_4\text{NBr}$, $(n\text{-C}_4\text{H}_9)_4\text{NClO}_4$, $(n\text{-C}_4\text{H}_9)_4\text{NI}$, $(\text{C}_2\text{H}_5)_4\text{N-maleate}$, $(\text{C}_2\text{H}_5)_4\text{N-benzoate}$ and $(\text{C}_2\text{H}_5)_4\text{N-phthalate}$ etc.; and organic ionic salts such as lithium stearylsulfonate, sodium octylsulfonate, and lithium dodecylbenzenesulfonate etc.; for example, may be mentioned. These ionic compounds may be used by being combined two or more kinds.

Concerning a compounding ratio of these ionic compounds, a ratio of the ionic compound to ether bond oxygen of the foregoing high-molecular compound is 0.0001 to 5.0 moles, especially a ratio of 0.005 to 2.0 moles is desirable. When a quantity of ionic compound is excessively large, the excessive ionic compound i.e. inorganic ionic salt for example, does not dissociate but is only present as a mixture, so that an ion conductivity is decreased conversely as a result. Further, a proper compounding ratio of the ionic compound differs depending on a kind of the electrode active material. For example, a ratio around a value offering the maximum ion conductivity of electrolyte is desirable for a battery utilizing the intercalation of layer compound, and a ratio must be set so as to cope with a change of ion concentration in the electrolyte caused by charging and discharging for a battery using electro-conductive polymer utilizing the doping phenomenon as the electrode active material.

There is no special limitation in an inclusion method of the ionic compound. A method may be mentioned, for example, in which the ionic compound is dissolved in an organic solvent such as methyl ethyl ketone or tetrahydrofuran etc. and mixed uniformly to the foregoing high-molecular compound, and the organic solvent is then removed under vacuum reduced pressure.

An organic compound which can dissolve the ionic compound may be included in the ion-conductive high-molecular compound. By doing so, the ion-conductive high-molecular compound can be improved markedly in its ionic conductivity without changing its basic skeleton.

As the organic compound which can dissolve the ionic compound; cyclic carbonic esters such as propylene carbonate and ethylene carbonate etc.; cyclic esters such as γ -butyrolactone; ethers such as tetrahydrofuran or its derivative, 1,3-dioxane, 1,2-dimethoxyethane and methyldigraim etc.; nitriles such as acetonitrile and benzonitrile etc.; dioxorane or its derivative; and sulfolane or its derivative etc.; for example, may be mentioned. These compounds may be used independently or by being combined two or more kinds. The kind of compound is not limited to them. Compounding ratio and compounding method are at will.

Carbon material may be used as the negative active material. The carbon material has a high doping capacity, a low self-discharge rate, an excellent cycle characteristic, and a base-potential extremely near to that of metallic lithium. A theoretically complicated chemical reaction does not take place at time of the electrochemical reaction during charging and discharging. Consequently, an extremely excellent charge/discharge cycle characteristic can be obtained when the carbon material is used as the negative active material. In addition, the anode becomes extremely stable from physical and electrochemical standpoints.

As the negative active material; alloys including lithium metal such as lithium-aluminum, lithium-lead, lithium-tin, lithium-aluminum-tin, lithium-gallium and Wood's alloys etc., lithium metals and carbon materials etc., may be mentioned. These materials may be used by being combined two or more kinds.

As the carbon material; it is desirable to use materials having analyzed results by diffraction of X-ray as listed in Table 1, carbon powder prepared by burning anisotropic pitch at a temperature of higher than $2,000^\circ\text{C}$ (average grain size: under $15\text{ }\mu\text{m}$ inclusive), and carbon fiber etc., for example.

Table 1

Lattice spacing (d002)	3.35~3.40Å
Size of crystalline in a-axis direction	La: 200Å or more
Size of crystalline in c-axis direction	Lc: 200Å or more
True density	2.00~2.25g/cm ³

As the positive active material, the following materials may be mentioned. There are I-group metallic compounds such as CuO, Cu₂O, Ag₂O, CuS and CuSO₄ etc.; IV-group metallic compounds such as TiS₂, SiO₂ and SnO etc.; V-group metallic compounds such as V₂O₅, V₆O₁₂, VO_x, Nb₂O₅, Bi₂O₃ and Sb₂O₃ etc.; VI-group metallic compounds such as CrO₃, Cr₂O₃, MoS₂, WO₃ and SeO₂ etc.; VII-group metallic compounds such as MnO₂ and Mn₂O₃ etc.; VIII-group metallic compounds such as Fe₂O₃, FeO, Fe₃O₄, Ni₂O₃, NiO, CoS₂ and CoO etc.; metallic compounds such as lithium-cobalt composite oxide and lithium-manganese composite oxide etc., for example, expressed by general formulas of Li_xMX₂ and Li_xMN_yX₂ (M and N are I- through VIII-group metals and X is chalcogens compound such as oxygen and sulfur etc.); electro-conductive high-molecular compounds such as polypyrrole, polyaniline, polyparaphenylene, polyacetylene and polyacene group materials; and pseudo-graphite structural carbon material etc. However, the kind of positive active material is not limited to them.

Concerning an installation method of the ion-conductive high-molecular compound on a surface of the electrode; it is desirable to coat the compound into an uniform thickness by means of, for example, a roller coating using an applicator roll, a doctor blade method, a spin coating and bar coder etc. However, the kind of coating method is not limited to them. By using these means, it become possible to coat the ion-conductive high-molecular compound on the surface of the electrode in a voluntary thickness and a voluntary shape.

Concerning an installation method of the electrode on the current collector; it is preferable to coat the compound into an uniform thickness by means of, for example, a roller coating using an applicator roll, a doctor blade method, a spin coating and bar coder etc. However, the kind of installation method is not limited to them. By using these means, it becomes possible to increase practical surface areas of the active material in contact with the electrolytes and current collector in the electrode, and it become possible to install the electrode on the current collectors in a voluntary thickness and a voluntary shape. In these cases, carbon such as graphite, carbon black and acetylene black etc. (This carbon has properties quite different from those of the carbon used for the negative active material.) and electro-conductive material such as metallic powder and electro-conductive metal oxide etc. are mixed in the electrode as occasion demands, so that an electron conductivity may be improved. Further, in order to obtain an uniform mixed and dispersed system when manufacturing the electrodes, several kinds of dispersants and dispersion mediums may be added. In addition, a thickener, an extender and a tackifier may be added.

It is preferable to use aluminum, stainless steel, titan and copper etc. for the positive current collector plate and to use stainless steel, iron, nickel and copper etc. for the negative current collector plate. However, the kind of material is not limited to them.

Brief Description of the Drawings

Fig. 1 is a vertical sectional view showing a fundamental structure of battery of this invention. Fig. 2 is a diagram showing discharge characteristics at initial stage and after long-term preservation for respective batteries embodiment 1 and comparison example 1. Fig. 3 is a diagram showing charge/discharge cycle characteristics at initial stage and after long-term preservation for respective batteries of embodiment 2 and comparison example 2. Fig. 4 is a diagram showing charge/discharge cycle characteristics at initial stage and after long-term preservation for respective batteries embodiment 3 and comparison example 3. Fig. 5 is a diagram showing discharge characteristics at initial stage for respective batteries embodiment 4 and comparison examples 4 and 5. Fig. 6 is a diagram showing discharge characteristics after long-term preservation for respective batteries embodiment 4 and comparison examples 4 and 5. Fig. 7 is a diagram showing discharge characteristics at initial stage for respective batteries embodiment 8 and comparison examples 3 and 6. Fig. 8 is a diagram showing discharge characteristics after long-term preservation for respective batteries embodiment 8 and comparison examples 3 and 6. Fig. 9 is a diagram showing discharge characteristics at initial stage and after long-term preservation for respective batteries embodiments 9 and 10 and comparison example 7. Fig. 10 is a diagram showing charge/discharge cycle

characteristics at initial stage and after long-term preservation for respective batteries embodiment 11 and comparison example 3. Fig. 11 is a vertical sectional view showing a fundamental structure of battery of embodiment 14. Fig. 12 is a diagram showing charge/discharge cycle characteristics at initial stage and after long-term preservation for respective batteries embodiments 16 and 17 and comparison example 9.

Best Mode for Carrying Out the Invention

(Embodiment 1)

Fig. 1 is a vertical sectional view showing a film type primary battery which is an example of battery of this invention. In this figure, 1 is a positive current collector plate comprising stainless steel, 2 is a cathode composite, 3 is an electrolyte layer, 4 is an anode, 5 is a negative current collector plate comprising stainless steel and 6 is a sealing material comprising denatured polypropylene. The both current collector plates 1 and 5 serve also as outer packages.

In the battery of this invention, palladium forming an element belonging to VIII-group in periodic table exists in the cathode composite 2.

The battery of this embodiment was made up through the following processes (a) to (d).

(a); The cathode composite 2 was formed in the following manner. MnO_2 forming the positive active material was mixed to acetylene black forming the conductive material with a weight ratio of 85 to 15 (mixture A_1). Polyethylene glycol diacrylate (molecular weight: 5000) was mixed to polyethylene glycol monoacrylate (molecular weight: 400) with a weight ratio of 6 to 4 to form a high-molecular mixture (mixture B_1). 10 weight parts of the mixture B_1 were mixed with 1 weight part of LiClO_4 , 20 weight parts of propylene carbonate and 0.2 weight part of palladium treated carbon (palladium content of 1.0%) (mixture C_1). Carbon having a brand name of "Palladium on 4- to 8-mesh carbon" made by Aldrich Corp. was used for the foregoing palladium treated carbon, which meant carbon of 4 to 8 meshes coated with palladium. The mixture A_1 was mixed to the mixture C_1 with a weight ratio of 10 to 3 under an atmosphere of dried inert gas (mixture D_1). The mixture D_1 was cast by means of screen coating on the positive current collector plate 1, on a surface of which a conductive carbon film is formed, and irradiated with electron beam having an electron beam intensity of 10 Mrad under an atmosphere of dried inert gas so as to be cured. A film thickness of the cathode composite 2 formed on the positive current collector plate 1 was 60 μm .

(b); The anode 4 was composed of lithium metal forming the negative active material, and formed by being press bonded to the negative current collector plate 5.

(c); The electrolyte layer 3 was formed on the anode 4 in the following manner. The mixture B_1 same with that of the process (a) was prepared. 30 weight parts of the mixture B_1 were mixed with 6 weight parts of LiClO_4 and 64 weight parts of propylene carbonate (mixture E_1). This mixture E_1 was cast by means of screen coating on the anode 4 and irradiated with electron beam having an electron beam intensity of 8 Mrad under the atmosphere of dried inert gas so as to be cured. A thickness of the electrolyte layer 3 formed on the anode 4 was 20 μm .

(d); A laminate of the cathode composite 2 and the positive current collector plate 1 prepared by the process (a) and a laminate of the electrolyte layer 3, the anode 4 and the negative current collector plate 5 prepared by the process (c) were made contact each other at the cathode composite 2 and the electrolyte layer 3.

In the processes (a) and (c), the mixture B_1 is polymerized by means of the irradiation of electron beam to form the ion-conductive high-molecular compound having a crosslink network structure. LiClO_4 forming the ionic compound is included in the prepared ion-conductive high-molecular compound under a state of being preferably dissolved by propylene carbonate.

(Comparison example 1)

A battery of this comparison example is different from that of the embodiment 1 only in a point that the cathode composite 2 does not include the palladium treated carbon.

(Test 1)

Discharge tests were done on the batteries of embodiment 1 and comparison example 1 to examine respective discharge characteristics at initial stage and after long-term preservation. An electrode surface area could be changed variously depending on manufacturing process, however, it was set to 100 cm^2 in

these tests.

Conditions of discharge tests were a temperature of 25 ° C, and a current per unit area of 0.1 mA/cm².

A period of long-term preservation was 100 days at 60 ° C.

Fig. 2 shows discharge characteristics at initial stage and after long-term preservation. In the figure, X1-
 5 (i) denotes a discharge characteristic at initial stage of the battery of embodiment 1, X1(p) denotes a discharge characteristic after long-term preservation of the battery of embodiment 1, Y1(i) denotes a discharge characteristic at initial stage of the battery of comparison example 1, and Y1(p) denotes a discharge characteristic after long-term preservation of the battery of comparison example 1. Further, an axis of abscissa represents a discharge time (hour) and an axis of ordinate represents a discharge voltage
 10 (V).

As obvious from Fig. 2, the battery of embodiment 1 is excellent in the discharge characteristics both at initial stage and after long-term preservation as compared with the battery of comparison example 1. This may be attributable to a fact that, since hydrogen gas produced in the battery is absorbed by the palladium included in the cathode composite 2 or added to the residual reactive double bond in the ion-conductive
 15 high-molecular compound included in the cathode composite 2 and the electrolyte layer 3, the rise of battery inside pressure is restrained and the expansion of battery is controlled so that contact of the electrolyte layer 3 with the cathode composite 2 and the anode 4 can be maintained in a desirable state.

Further, respective 25 cells of the batteries of embodiment 1 and comparison example 1 were examined to check numbers of expanded cells after long-term preservation. The number was zero for the
 20 battery of embodiment 1, but it was seven for the battery of comparison example 1. In other words, no expansion was recognized in case of the battery of embodiment 1.

(Embodiment 2)

25 This embodiment relates to a film type secondary battery. In the battery of this embodiment, V₂O₅ is used for the active material of the cathode composite 2, and palladium forming an element belonging to VIII-group in periodic table exists in the cathode composite 2. A battery structure is same with that of the battery shown in Fig. 1.

The battery of this embodiment was made up through the following processes (a) to (d).

30 (a); The cathode composite 2 was formed in the following manner. V₂O₅ forming the positive active material was mixed to acetylene black forming the conductive material with a weight ratio of 85 to 15 (mixture A₂). While, the mixture B₁ same with that of the embodiment 1 was prepared. 10 weight parts of the mixture B₁ were mixed with 1 weight part of LiAsF₆, 10 weight parts of ethylene carbonate, 10 weight parts of 2-methyltetrahydrofuran and 0.2 weight part of palladium treated carbon same with that of the
 35 embodiment 1 (mixture C₂). The mixture A₂ was mixed to the mixture C₂ with a weight ratio of 10 to 3 under an atmosphere of dried inert gas (mixture D₂). The mixture D₂ was cast by means of screen coating on the positive current collector plate 1, on a surface of which a conductive carbon film is formed, and irradiated with electron beam having an electron beam intensity of 10 Mrad under an atmosphere of dried inert gas so as to be cured. A film thickness of the cathode composite 2 formed on
 40 the positive current collector plate 1 was 60 μm.

(b); The anode 4 was composed of lithium metal forming the negative active material, and formed by being press bonded to the negative current collector plate 5.

(c); The electrolyte layer 3 was formed on the anode 4 in the following manner. The mixture B₁ same with that of the embodiment 1 was prepared. 30 weight parts of the mixture B₁ were mixed with 6 weight
 45 parts of LiAsF₆, 32 weight parts of ethylene carbonate and 32 weight parts of 2-methyltetrahydrofuran (mixture E₂). This mixture E₂ was cast by means of screen coating on the anode 4, and irradiated with electron beam having an electron beam intensity of 8 Mrad under the atmosphere of dried inert gas so as to be cured. A thickness of the electrolyte layer 3 formed on the anode 4 was 20 μm.

(d); A laminate of the cathode composite 2 and the positive current collector plate 1 prepared by the
 50 process (a) and a laminate of the electrolyte layer 3, the anode 4 and the negative current collector plate 5 prepared by the process (c) were made contact each other at the cathode composite 2 and the electrolyte layer 3.

(Comparison example 2)

55 A battery of this comparison example is different from that of the embodiment 2 only in a point that the cathode composite 2 does not include the palladium treated carbon.

(Test 2)

Charge/discharge cycle tests were done on the batteries of embodiment 2 and comparison example 2 to examine respective charge/discharge cycle characteristics at initial stage and after long-term preservation. An electrode surface area could be changed variously depending on manufacturing process, however, it was set to 100 cm² in these tests.

Conditions of charge/discharge cycle tests were a temperature of 25 °C, a constant current per unit area of 50 μA/cm², a charge end voltage of 3.2V and a discharge end voltage of 2.0V.

A period of long-term preservation was 100 days at 60 °C.

Fig. 3 shows charge/discharge cycle characteristics at initial stage and after long-term preservation. In the figure, X2(i) denotes a charge/discharge cycle characteristic at initial stage of the battery of embodiment 2, X2(p) denotes a charge/discharge cycle characteristic after long-term preservation of the battery of embodiment 2, Y2(i) denotes a charge/discharge cycle characteristic at initial stage of the battery of comparison example 2 and Y2(p) denotes a charge/discharge cycle characteristic after long-term preservation of the battery of comparison example 2. Further, an axis of abscissa represents a charge/discharge cycle number (time) and an axis of ordinate represents a battery capacity (mAh).

As obvious from Fig. 3, the battery of embodiment 2 is excellent in the charge/discharge cycle characteristics both at initial stage and after long-term preservation as compared with the battery of comparison example 2. The reason can be considered as same with that of the embodiment 1.

Further, respective 25 cells of the batteries of embodiment 2 and comparison example 2 were examined to check numbers of expanded cells after long-term preservation. The number was zero for the battery of embodiment 2, but it was five for the battery of comparison example 2. In other words, no expansion was recognized in case of the battery of embodiment 2.

(Embodiment 3)

This embodiment relates to a film type secondary battery. In the battery of this embodiment, LiCoO₂ is used for the active material of the cathode composite 2. A anode composite is used in place of the anode of the battery shown in Fig. 1, and other structure is same with that of the battery shown in Fig. 1. Palladium forming an element belonging to VIII-group in periodic table exists in the cathode composite 2 and the anode composite 4. An aluminium plate is used for the positive current collector plate 1.

The battery of this embodiment was made up through the following processes (a) to (e).

(a); The cathode composite 2 was formed in the following manner. LiCoO₂ forming the positive active material was mixed to acetylene black forming the conductive material with a weight ratio of 85 to 15 (mixture A₃). While, the mixture B₁ same with that of the embodiment 1 was prepared. 10 weight parts of the mixture B₁ were mixed with 1 weight part of LiBF₄, 10 weight parts of 1,2-dimethoxyethane, 10 weight parts of γ-butyrolactone and 0.2 weight part of palladium treated carbon same with that of the embodiment 1 (mixture C₃). The mixture A₃ was mixed to the mixture C₃ with a weight ratio of 10 to 3 under an atmosphere of dried inert gas (mixture D₃). The mixture D₃ was cast by means of screen coating on the positive current collector plate 1, on a surface of which a conductive carbon film is formed, and irradiated with electron beam having an electron beam intensity of 12 Mrad under an atmosphere of dried inert gas so as to be cured. A film thickness of the cathode composite 2 formed on the positive current collector plate 1 was 60 μm.

(b); The electrolyte layer 3 was formed on the cathode composite 2 in the following manner. The mixture B₁ same with that of the embodiment 1 was prepared. 30 weight parts of the mixture B₁ were mixed with 6 weight parts of LiBF₄, 32 weight parts of 1,2-dimethoxyethane and 32 weight parts of γ-butyrolactone (mixture F₃). The mixture F₃ was cast by means of screen coating on the cathode composite 2 and irradiated with electron beam having an electron beam intensity of 8 Mrad under an atmosphere of dried inert gas so as to be cured. A film thickness of the electrolyte layer 3 formed on the cathode composite 2 was 25 μm.

(c); The anode composite 4 was formed in the following manner. The mixture C₃ same with that of the process (a) was prepared. Carbon powder forming the negative active material was mixed to the mixture C₃ with a weight ratio of 8 to 2 under an atmosphere of dried inert gas (mixture G₃). The mixture G₃ was cast by means of screen coating on the negative current collector plate 5 and irradiated with electron beam having an electron beam intensity of 15 Mrad under an atmosphere of dried inert gas so as to be cured. A film thickness of the anode composite 4 formed on the negative current collector plate 5 was 30 μm.

(d); The electrolyte layer 3 was formed on the anode composite 4 in the following manner. The mixture F_3 same with that of the process (b) was prepared. The mixture F_3 was cast by means of screen coating on the anode composite 4 and irradiated with electron beam having an electron beam intensity of 8 Mrad under an atmosphere of dried inert gas so as to be cured. A thickness of the electrolyte layer 3 formed on the anode composite 4 was 25 μm .

(e); A laminate of electrolyte layer 3, the cathode composite 2 and the positive current collector plate 1 prepared by the process (b) and a laminate of the electrolyte layer 3, the anode composite 4 and the negative current collector plate 5 prepared by the process (d) were made contact each other at the respective electrolyte layers 3.

(Comparison example 3)

A battery of this comparison example is different from that of the embodiment 3 only in a point that the cathode composite 2 and the anode composite 4 do not include the palladium treated carbon.

(Test 3)

Charge/discharge cycle tests were done on the batteries of embodiment 3 and comparison example 3 to examine respective charge/discharge cycle characteristics at initial stage and after long-term preservation. An electrode surface area could be changed variously depending on manufacturing process, however, it was set to 100 cm^2 in these tests.

Conditions of charge/discharge cycle tests were a temperature of 25 °C, a constant current per unit area of 50 $\mu\text{A}/\text{cm}^2$, a charge end voltage of 4.1V and a discharge end voltage of 2.7V.

A period of long-term preservation was 100 days at 60 °C.

Fig. 4 shows charge/discharge cycle characteristics at initial stage and after long-term preservation. In the figure, X3(i) denotes a charge/discharge cycle characteristic at initial stage of the battery of embodiment 3, X3(p) denotes a charge/discharge cycle characteristic after long-term preservation of the battery of embodiment 3, Y3(i) denotes a charge/discharge cycle characteristic at initial stage of the battery of comparison example 3 and Y3(p) denotes a charge/discharge cycle characteristic after long-term preservation of the battery of comparison example 3. Further, an axis of abscissa represents a charge/discharge cycle number (time) and an axis of ordinate represents a battery capacity (mAh).

As obvious from Fig. 4, the battery of embodiment 3 is excellent in the charge/discharge cycle characteristics both at initial stage and after long-term preservation as compared with the battery of comparison example 3. The reason can be considered as same with that of the embodiment 1.

Further, respective 40 cells of the batteries of embodiment 3 and comparison example 3 were examined to check numbers of expanded cells after long-term preservation. The number was zero for the battery of embodiment 3, but it was 17 for the battery of comparison example 3. In other words, no expansion was recognized in case of the battery of embodiment 3.

(Embodiment 4)

This embodiment relates to a film type primary battery and a battery structure is same with the battery shown in Fig. 1. Palladium forming an element belonging to VIII-group in periodic table and a binder exist in the cathode composite 2.

The battery of this embodiment was made up through the following processes (a) to (e).

(a); The cathode composite 2 was formed in the following manner. The mixture A_1 same with that of the embodiment 1 was prepared. The mixture A_1 was mixed to xylene solution (2 weight parts solution) of nitrile-butadiene rubber forming the binder and the palladium treated carbon same with that of the embodiment 1 with a weight ratio of 2.2 to 2.0 to 0.04 under an atmosphere of dried inert gas. This mixture was cast on the positive current collector plate 1, on a surface of which a conductive carbon film was formed, by means of screen coating and dried under the atmosphere of dried inert gas so as to be cured. A film thickness of the cathode composite 2 formed on the positive current collector plate 1 was 60 μm .

(b); The electrolyte layer 3 was formed on the cathode composite 2 in the following manner. The mixture E_1 same with that of the embodiment 1 was prepared. This mixture E_1 was cast by means of screen coating on the cathode composite 2, and irradiated with electron beam having an electron beam intensity of 8 Mrad under the atmosphere of dried inert gas so as to be cured. A film thickness of the electrolyte layer 3 formed on the cathode composite 2 was 15 μm .

(c); The anode 4 was composed of lithium metal forming the negative active material, and formed by being press bonded to the negative current collector plate 5.

(d); The electrolyte layer 3 was formed on the anode 4 in the following manner. The mixture E₁ same with that of the embodiment 1 was prepared. This mixture E₁ was cast by means of screen coating on the anode 4, and irradiated with electron beam having an electron beam intensity of 8 Mrad under the atmosphere of dried inert gas so as to be cured. A film thickness of the electrolyte layer 3 formed on the anode 4 was 15 μm .

(e); A laminate of the electrolyte layer 3, the cathode composite 2 and the positive current collector plate 1 prepared by the process (b) and a laminate of the electrolyte layer 3, the anode 4 and the negative current collector plate 5 prepared by the process (d) were made contact each other at the respective electrolyte layers 3.

(Comparison example 4)

A battery of this comparison example is different from that of the comparison example 1 only in a point that the thickness of the electrolyte layer 3 is 30 μm . Namely, the cathode composite 2 does not include the palladium treated carbon and the binder.

(Comparison example 5)

A battery of this comparison example is different from that of the embodiment 4 only in a point that the cathode composite 2 includes the binder but does not include the palladium treated carbon and that the electrolyte layer 3 is formed by irradiation of ultraviolet ray.

The battery of this comparison example was made up through the following processes (a) to (e).

(a); The cathode composite 2 was formed in the following manner. The same process (a) of the embodiment 4 was applied except that the palladium treated carbon was omitted. A film thickness of the cathode composite 2 formed on the positive current collector plate 1 was 60 μm .

(b); The electrolyte layer 3 was formed on the cathode composite 2 in the following manner. The mixture B₁ same with that of the embodiment 1 was prepared. 30 weight parts of mixture B₁ was mixed to 6 weight parts of LiClO₄, 64 weight parts of propylene carbonate and 0.03 weight part of benzylmethylketal (mixture I₅). This mixture I₅ was cast by means of screen coating on the cathode composite 2, and irradiated with ultraviolet ray having an intensity of 20 mW/cm² for 60 seconds under the atmosphere of dried inert gas so as to be cured. A film thickness of the electrolyte layer 3 formed on the cathode composite 2 was 15 μm .

(c); The anode 4 was composed of lithium metal forming the negative active material, and formed by being press bonded to the negative current collector plate 5.

(d); The electrolyte layer 3 was formed on the anode 4 in the following manner. The mixture I₅ same with that of the process (b) was prepared. This mixture I₅ was cast by means of screen coating on the anode 4, and irradiated with ultraviolet ray having an intensity of 20 mW/cm² for 60 seconds under the atmosphere of dried inert gas so as to be cured. A film thickness of the electrolyte layer 3 formed on the anode 4 was 15 μm .

(e); A laminate of the electrolyte layer 3, the cathode composite 2 and the positive current collector plate 1 prepared by the process (b) and a laminate of the electrolyte layer 3, the anode 4 and the negative current collector plate 5 prepared by the process (d) were made contact each other at the respective electrolyte layers 3.

(Test 4)

Discharge tests were done on the batteries of embodiment 4 and comparison examples 4 and 5 using same test conditions with those of the test 1, to examine respective discharge characteristics at initial stage and after long-term preservation. Fig. 5 shows discharge characteristics at initial stage and Fig. 6 shows discharge characteristics after long-term preservation. In these figures, X4 denotes a discharge characteristic of the battery of embodiment 4, and Y4 and Y5 denotes discharge characteristics of the batteries of comparison examples 4 and 5 respectively. Further, an axis of abscissa represents a discharge time (hour) and an axis of ordinate represents a discharge voltage (V).

As obvious from Fig. 5 and Fig. 6, the battery of embodiment 4 is excellent in the discharge characteristics both at initial stage and after long-term preservation as compared with the batteries of comparison examples 4 and 5. The reason can be considered as same with that of the embodiment 1.

Further, respective 40 cells of the batteries of embodiment 4 and comparison examples 4 and 5 were examined to check numbers of expanded cells after long-term preservation. The number was zero for the battery of embodiment 4, but it was nine for the battery of comparison example 4 and 13 for the battery of comparison example 5. In other words, no expansion was recognized in case of the battery of embodiment 4.

(Embodiment 5)

A battery of this embodiment is different from that of the embodiment 4 only in a point that the cathode composite 2 was formed in the following manner.

The mixture A₁ same with that of the embodiment 1 was prepared. The mixture A₁ was mixed to xylene solution (2 weight parts solution) of nitrile-butadiene rubber forming the binder and platinum treated carbon with a weight ratio of 2.2 to 2.0 to 0.06 under the atmosphere of dried inert gas. This mixture was cast on the positive current collector plate 1, on a surface of which a conductive carbon film was formed, by means of screen coating and dried under the atmosphere of dried inert gas so as to be cured. A film thickness of the cathode composite 2 formed on the positive current collector plate 1 was 60 μm. Carbon having a brand name of "Platinum on 4- to 8-mash carbon" made by Aldrich Corp. was used for the platinum treated carbon. This meant carbon of 4 to 8 meshes coated with platinum.

(Embodiment 6)

A battery of this embodiment is different from that of the embodiment 4 only in a point that the cathode composite 2 was formed in the following manner.

The mixture A₁ same with that of the embodiment 1 was prepared. The mixture A₁ was mixed to xylene solution (2 weight parts solution) of nitrile-butadiene rubber forming the binder and ruthenium treated carbon with a weight ratio of 2.2 to 2.0 to 0.05 under the atmosphere of dried inert gas. This mixture was cured in the same way as that of the embodiment 5. A film thickness of the cathode composite 2 formed on the positive current collector plate 1 was 60 μm. Carbon having a brand name of "Ruthenium on 4- to 8-mash carbon" made by Aldrich Corp. was used for the ruthenium treated carbon. This meant carbon of 4 to 8 meshes coated with ruthenium.

(Embodiment 7)

A battery of this embodiment is different from that of the embodiment 4 only in a point that the cathode composite 2 was formed in the following manner.

The mixture A₁ same with that of the embodiment 1 was prepared. The mixture A₁ was mixed to xylene solution (2 weight parts solution) of nitrile-butadiene rubber forming the binder and rhodium treated carbon with a weight ratio of 2.2 to 2.0 to 0.05. This mixture was cured in the same way as that of the embodiment 5. A film thickness of the cathode composite 2 formed on the positive current collector plate 1 was 60 μm. Carbon having a brand name of "Rhodium on 4- to 8-mash carbon" made by Aldrich Corp. was used for the rhodium treated carbon. This meant carbon of 4 to 8 meshes coated with rhodium.

(Test 5)

Respective 40 cells of the batteries of embodiments 5, 6 and 7 were examined to check numbers of expanded cells after 100 days preservation at 60 °C i.e. after long-term preservation. The number was zero for the battery of embodiment 5, but it was one for the batteries 6 and 7 respectively. In other words, the expansion could be restrained even when platinum, ruthenium and rhodium were included in place of palladium.

(Embodiment 8)

This embodiment relates to a film type secondary battery. In the battery of this embodiment, LiCoO₂ is used for the active material of the cathode composite 2. An anode composite is used in place of the anode of the battery shown in Fig. 1, and other components are same with those of the battery shown in Fig. 1. Palladium forming an element belonging to VIII-group in periodic table and the binder exist in the cathode composite 2 and the anode composite 4. An aluminum plate is used for the positive current collector plate 1.

The battery of this embodiment was made up through the following processes (a) to (e).

(a); The cathode composite 2 was formed in the following manner. The mixture A₃ same with that of the embodiment 3 was prepared. The mixture A₃ was mixed to dimethylformamide solution (2 wt% solution) of polyacrylonitrile forming the binder and the palladium treated carbon same with that of the embodiment 1 with a weight ratio of 2.4 to 2.0 to 0.04 under the atmosphere of dried inert gas. This mixture was cast on the positive current collector plate 1, on a surface of which a conductive carbon film was formed, by means of screen coating and dried under the atmosphere of dried inert gas so as to be cured. A film thickness of the cathode composite 2 formed on the positive current collector plate 1 was 60 μm .

(b); The electrolyte layer 3 was formed on the cathode composite 2 in the following manner. The mixture F₃ same with that of the embodiment 3 was prepared. This mixture F₃ was cast by means of screen coating on the cathode composite 2 under the atmosphere of dried inert gas, and irradiated with electron beam having an electron beam intensity of 8 Mrad under the atmosphere of dried inert gas so as to be cured. A film thickness of the electrolyte layer 3 formed on the cathode composite 2 was 25 μm .

(c); The anode composite 4 was formed in the following manner. Carbon powder forming the negative active material, toluene solution (2 weight parts solution) of copolymer of ethylene-propylene-cyclopentadiene and the palladium treated carbon same with that of the embodiment 1 were mixed with a weight ratio of 2.0 to 5.0 to 0.025 under the atmosphere of dried inert gas. This mixture was cast on the negative current collector plate 5 by means of screen coating, and dried under the atmosphere of dried inert gas so as to be cured. A film thickness of the anode composite 4 formed on the negative current collector plate 5 was 30 μm .

(d); The electrolyte layer 3 was formed on the anode composite 4 in the following manner. The mixture F₃ same with that of the embodiment 3 was prepared. This mixture F₃ was cast by means of screen coating on the anode composite 4 under the atmosphere of dried inert gas, and irradiated with electron beam having an electron beam intensity of 8 Mrad under the atmosphere of dried inert gas so as to be cured. A film thickness of the electrolyte layer 3 formed on the anode composite 4 was 25 μm .

(e); A laminate of the electrolyte layer 3, the cathode composite 2 and the positive current collector plate 1 prepared by the process (b) and a laminate of the electrolyte layer 3, the anode composite 4 and the negative current collector plate 5 prepared by the process (d) were made contact each other at the respective electrolyte layers 3.

(Comparison example 6)

A battery of this comparison example is different from that of the embodiment 8 only in a point that the cathode composite 2 and the anode composite 4 include the binder but they do not include the palladium treated carbon, and that the electrolyte layer 3 is formed by the irradiation of ultraviolet ray.

The battery of this comparison example was made up through the following processes (a) to (e).

(a); The cathode composite 2 was formed in the following manner. The same process (a) of the embodiment 8 was applied except that the palladium treated carbon was omitted. A film thickness of the cathode composite 2 formed on the positive current collector plate 1 was 60 μm .

(b); The electrolyte layer 3 was formed on the cathode composite 2 in the following manner. The mixture B₁ same with that of the embodiment 1 was prepared. 30 weight parts of mixture B₁ was mixed to 6 weight parts of LiBF₄, 32 weight parts of 1,2-dimethoxyethane, 32 weight parts of γ -butyrolactone and 0.03 weight part of benzylmethylketal (mixture I₆). This mixture I₆ was cast by means of screen coating on the cathode composite 2 under the atmosphere of dried inert gas, and irradiated with ultraviolet ray having an intensity of 20 mW/cm² for 60 seconds under the atmosphere of dried inert gas so as to be cured. A film thickness of the electrolyte layer 3 formed on the cathode composite 2 was 25 μm .

(c); The anode composite 4 was formed in the following manner. The same process (c) of the embodiment 8 was applied except that the palladium treated carbon was omitted. A film thickness of the anode composite 4 formed on the negative current collector plate 5 was 30 μm .

(d); The electrolyte layer 3 was formed on the anode composite 4 in the following manner. The mixture I₆ same with that of the process (b) was prepared. This mixture I₆ was cast by means of screen coating on the anode composite 4 under the atmosphere of dried inert gas, and irradiated with ultraviolet ray having an intensity of 20 mW/cm² for 60 seconds under the atmosphere of dried inert gas so as to be cured. A film thickness of the electrolyte layer 3 formed on the anode composite 4 was 25 μm .

(e); A laminate of the electrolyte layer 3, the cathode composite 2 and the positive current collector plate 1 prepared by the process (b) and a laminate of the electrolyte layer 3, the anode 4 and the negative current collector plate 5 prepared by the process (d) were made contact each other at the respective electrolyte layers 3.

(Test 6)

Charge/discharge cycle tests were done on the batteries of embodiment 8 and comparison examples 3 and 6 using same test conditions with those of the test 3, to examine respective charge/discharge cycle characteristics at initial stage and after long-term preservation.

Fig. 7 shows charge/discharge cycle characteristics at initial stage and Fig. 8 shows charge/discharge cycle characteristics after long-term preservation. In these figures, X8 denotes a charge/discharge cycle characteristic of the battery of embodiment 8, Y3 denotes a charge/discharge cycle characteristic of the battery of comparison example 3 and Y6 denotes a charge/discharge cycle characteristic after long-term preservation of the battery of comparison example 6. Further, an axis of abscissa represents a charge/discharge cycle number (time) and an axis of ordinate represents a battery capacity (mAh).

As obvious from Fig. 7 and Fig. 8, the battery of embodiment 8 is excellent in the charge/discharge cycle characteristics both at initial stage and after long-term preservation as compared with the batteries of comparison examples 3 and 6. The reason can be considered as same with that of the embodiment 1.

Further, respective 40 cells of the batteries of embodiment 8 and comparison examples 3 and 6 were examined to check numbers of expanded cells after long-term preservation. The number was zero for the battery of embodiment 8, but it was nine for the battery of comparison example 3 and 13 for the battery of comparison example 6. In other words, no expansion was recognized in case of the battery of embodiment 8.

(Embodiment 9)

This embodiment relates to a film type primary battery. A battery structure is same with that of the battery shown in Fig. 1. Palladium forming an element belonging to VIII-group in periodic table exists in the cathode composite 2.

The battery of this embodiment was made up through the following processes (a) to (d).

(a); The cathode composite 2 was formed in the following manner. The mixture A₂ same with that of the embodiment 2 was prepared. While, the mixture C₁ same with that of the embodiment 1 was prepared. The mixture A₂ was mixed to the mixture C₁ with a weight ratio of 10 to 3 under the atmosphere of dried inert gas. This mixture was cast by means of screen coating on the positive current collector plate 1, on a surface of which a conductive carbon film was formed, and irradiated with electron beam having an electron beam intensity of 10 Mrad under the atmosphere of dried inert gas so as to be cured. A film thickness of the cathode composite 2 formed on the positive current collector plate 1 was 60 μ m.

(b); The anode 4 was composed of lithium metal forming the negative active material, and formed by being press bonded to the negative current collector plate 5.

(c); The electrolyte layer 3 was formed on the anode 4 in the following manner. The mixture E₁ same with that of the embodiment 1 was prepared. This mixture E₁ was cast by means of screen coating on the anode 4, and irradiated with electron beam having an electron beam intensity of 8 Mrad under the atmosphere of dried inert gas so as to be cured. A thickness of the electrolyte layer 3 formed on the anode 4 was 20 μ m.

(d); A laminate of the cathode composite 2 and the positive current collector plate 1 prepared by the process (a) and a laminate of the electrolyte layer 3, the anode 4 and the negative current collector plate 5 prepared by the process (c) were made contact each other at the cathode composite 2 and the electrolyte layer 3.

(Comparison example 7)

A battery of this comparison example is different from that of the embodiment 9 only in a point that the cathode composite 2 does not include the palladium treated carbon.

(Embodiment 10)

This embodiment relates to a film type primary battery and a battery structure is same with that of the battery shown in Fig. 1. In the battery of this embodiment, palladium forming an element belonging to VIII-group in periodic table exists in the electrolyte layer 3, and a binder exists in the cathode composite 2.

The battery of this embodiment was made up through the following processes (a) to (e).

(a); The cathode composite 2 was formed in the following manner. The mixture A₁ same with that of the embodiment 1 was prepared. The mixture A₁ was mixed to xylene solution (2 weight parts solution) of

nitrile-butadiene rubber with a weight ratio of 2.2 to 2.0 under the atmosphere of dried inert gas. This mixture was cast by means of screen coating on the positive current collector plate 1, on a surface of which a conductive carbon film was formed, and dried under the atmosphere of dried inert gas so as to be cured. A film thickness of the cathode composite 2 formed on the positive current collector plate 1 was 60 μm .

(b); The electrolyte layer 3 was formed on the cathode composite 2 in the following manner. The mixture B₁ same with that of the embodiment 1 was prepared. 30 weight parts of the mixture B₁ were mixed to 6 weight parts of LiClO₄, 64 weight parts of propylene carbonate and 1.4 weight parts of palladium treated carbon same with that of the embodiment 1. This mixture was cast by means of screen coating on the cathode composite 2, and irradiated with electron beam having an electron beam intensity of 8 Mrad under the atmosphere of dried inert gas so as to be cured. A thickness of the electrolyte layer 3 formed on the cathode composite 2 was 15 μm .

(c); The anode 4 was composed of lithium metal forming the negative active material, and formed by being press bonded to the negative current collector plate 5.

(d); The electrolyte layer 3 was formed on the anode 4 in the following manner. The mixture E₁ same with that of the embodiment 1 was prepared. This mixture E₁ was cast by means of screen coating on the anode 4, and irradiated with electron beam having an electron beam intensity of 8 Mrad under the atmosphere of dried inert gas so as to be cured. A thickness of the electrolyte layer 3 formed on the anode 4 was 15 μm .

(e); A laminate of the electrolyte layer 3, the cathode composite 2 and the positive current collector plate 1 prepared by the process (b) and a laminate of the electrolyte layer 3, the anode 4 and the negative current collector plate 5 prepared by the process (d) were made contact each other at the respective electrolyte layers 3.

(Test 7)

Discharge tests were done on the batteries of embodiments 9 and 10 and comparison example 7 using the same conditions as those of the test 1, to examine respective discharge characteristics at initial stage and after long-term preservation. Fig. 9 shows discharge characteristics at initial stage and after long-term preservation. In the figure, X9(i) and X10(i) denote discharge characteristics at initial stage of the batteries of embodiments 9 and 10, X9(p) and X10(p) denote discharge characteristics after long-term preservation of the batteries of embodiments 9 and 10, Y7(i) denotes a discharge characteristic at initial stage of the battery of comparison example 7 and Y7(p) denotes a discharge characteristic after long-term preservation of the battery of comparison example 7. Further, an axis of abscissa represents a discharge time (hour) and an axis of ordinate represents a discharge voltage (V).

As obvious from Fig. 9, the batteries of embodiments 9 and 10 are excellent in the discharge characteristics both at initial stage and after long-term preservation as compared with the batteries of comparison example 7. The reason can be considered as same with that of the embodiment 1.

Further, respective 25 cells of the batteries of embodiments 9 and 10 and comparison example 7 were examined to check numbers of expanded cells after long-term preservation. The number was zero for the batteries of embodiments 9 and 10, but it was seven for the battery of comparison example 7. In other words, no expansion was recognized in case of the batteries of embodiments 9 and 10.

(Embodiment 11)

This embodiment relates to a film type secondary battery. In the battery of this embodiment, LiCoO₂ is used for the active material of the cathode composite 2. An anode composite is used in place of the anode for the battery shown in Fig. 1, and other components are same with those of the battery shown in Fig. 1. In the battery of this embodiment, palladium forming an element belonging to VIII-group in periodic table exists in the electrolyte layer 3. Further, a binder exists in the cathode composite 2 and the anode composite 4. An aluminum plate is used for the positive current collector plate 1.

The battery of this embodiment was made up through the following processes (a) to (e).

(a); The cathode composite 2 was formed in the following manner. The mixture A₃ same with that of the embodiment 3 was prepared. The mixture A₃ was mixed to dimethylformamide solution (2 wt% solution) of polyacrylonitrile forming the binder with a weight ratio of 2.4 to 2.0 under the atmosphere of dried inert gas. This mixture was cast by means of screen coating on the positive current collector plate 1, on a surface of which a conductive carbon film was formed, and dried under the atmosphere of dried inert gas so as to be cured. A film thickness of the cathode composite 2 formed on the positive current collector

plate 1 was 60 μm .

(b); The electrolyte layer 3 was formed on the cathode composite 2 in the following manner. The mixture B₁ same with that of the embodiment 1 was prepared. 30 weight parts of the mixture B₁ were mixed to 6 weight parts of LiBF₄, 32 weight parts of 1,2-dimethoxyethane, 32 weight parts of γ -butyrolactone and 1.5 weight parts of palladium treated carbon same with that of the embodiment 1. This mixture was cast by means of screen coating on the cathode composite 2, and irradiated with electron beam having an electron beam intensity of 8 Mrad under the atmosphere of dried inert gas so as to be cured. A thickness of the electrolyte layer 3 formed on the cathode composite 2 was 25 μm .

(c); The anode composite 4 was formed in the following manner. Carbon powder forming the negative active material and toluene solution (2 weight parts solution) of copolymer of ethylene-propylene-cyclopentadiene were mixed with a weight ratio of 2.0 to 5.0 under the atmosphere of dried inert gas. This mixture was cast by means of screen coating on the negative current collector plate 5 and dried under the atmosphere of dried inert gas so as to be cured. A film thickness of the anode composite 4 formed on the negative current collector plate 5 was 30 μm .

(d); The electrolyte layer 3 was formed on the anode composite 4 in the following manner. The mixture F₃ same with that of the embodiment 3 was prepared. This mixture F₃ was cast by means of screen coating on the anode composite 4 under the atmosphere of dried inert gas, and irradiated with electron beam having an electron beam intensity of 8 Mrad under the atmosphere of dried inert gas so as to be cured. A film thickness of the electrolyte layer 3 formed on the anode composite 4 was 25 μm .

(e); A laminate of the electrolyte layer 3, the cathode composite 2 and the positive current collector plate 1 prepared by the process (b) and a laminate of the electrolyte layer 3, the anode composite 4 and the negative current collector plate 5 prepared by the process (d) were made contact each other at the respective electrolyte layers 3.

25 (Test 8)

Charge/discharge cycle test was done on the battery of embodiment 11 using the same conditions as those of the test 3, to examine charge/discharge cycle characteristics at initial stage and after long-term preservation. Fig. 10 shows charge/discharge cycle characteristics at initial stage and after long-term preservation. Further, cycle characteristics of the battery of comparison example 3 are also shown in the figure. In these figures, X11(i) denotes a discharge characteristic at initial stage of the battery of embodiment 11, X11(p) denotes a discharge characteristic after long-term preservation of the battery of embodiment 11, Y3(i) denotes a discharge characteristic at initial stage of the battery of comparison example 3, and Y3(p) denotes a discharge characteristic after long-term preservation of the battery of comparison example 3. Further, an axis of abscissa represents a discharge time (hour) and an axis of ordinate represents a discharge voltage (V).

As obvious from Fig. 10, the battery of embodiment 11 is excellent in the discharge characteristics both at initial stage and after long-term preservation as compared with the battery of comparison example 3. The reason can be considered as same with that of the embodiment 1.

Further, 25 cells of the battery of embodiment 11 were examined to check numbers of expanded cells after long-term preservation. The number was zero for the battery of embodiment 11. In other words, no expansion was recognized in case of the battery of embodiment 11.

(Embodiment 12)

In a battery of this embodiment; the palladium treated carbon same with that of the embodiment 1 was installed on a surface of the anode 4 composed of lithium metal, the palladium treated carbon was omitted in the cathode composite 2, and the other components were same with those of the embodiment 9.

50 (Embodiment 13)

In a battery of this embodiment; the palladium treated carbon same with that of the embodiment 1 was installed between the cathode composite 2 and the electrolyte layer 3, the palladium treated carbon was omitted in the cathode composite 2, and the other components were same with those of the embodiment 9.

(Embodiment 14)

In a battery of this embodiment; the palladium treated carbon same with that of the embodiment 1 was installed on a surface of the sealing material 6 as illustrated by Fig. 11, the palladium treated carbon was omitted in the cathode composite 2, and the other components were same with those of the embodiment 9. In Fig. 11, 7 is the palladium treated carbon and the other components are same with those of Fig. 1.

(Embodiment 15)

A battery of this embodiment relates to a film type primary battery and is made up in the following manner.

85 weight parts of MnO_2 forming the positive active material, 7 weight parts of acetylene black forming the conductive material, 5 weight parts of polytetrafluoroethylene forming the binder, and 3 weight parts of palladium treated carbon same with that of the embodiment 1 were mixed, so that a composite sheet having a thickness of 0.2 mm comprising the mixture was formed. While, a stainless foil on a periphery of which denatured polypropylene forming the sealing material was installed, was prepared. The foregoing composite sheet was press bonded onto the stainless foil to prepare the cathode.

On the other hand, a lithium foil having a thickness of about 0.1 mm was press bonded to the stainless foil to prepare the anode. An electrolyte comprising propylene carbonate solution dissolved with LiClO_4 of 1 mol. was impregnated under reduced pressure to a separator comprising polypropylene non-woven fabric and the cathode.

The cathode, the separator and the anode were laminated, and the peripheral sealing material was heat sealed to complete the battery.

(Comparison example 8)

In a battery of this comparison example; the amount of acetylene black in the composite sheet of cathode was 10 weight parts, the palladium treated carbon was omitted, and the other components were same with those of the embodiment 15.

(Test 9)

Respective 25 cells of the batteries of embodiments 12 through 15 and comparison example 8 were examined to check numbers of expanded cells after 100 days preservation at 60°C i.e. after long-term preservation. The number was zero for the batteries of embodiments 12 through 15, but it was ten for the battery of comparison example 8. In other words, no expansion was recognized in case of the batteries of embodiment 12 through 15.

(Embodiment 16)

A battery of this embodiment relates to a film type secondary battery and is made up in the following manner.

85 weight parts of LiCoO_2 forming the positive active material, 7 weight parts of acetylene black forming the conductive material, 5 weight parts of polytetrafluoroethylene forming the binder, and 3 weight parts of palladium treated carbon same with that of the embodiment 1 were mixed, so that a composite sheet having a thickness of 0.2 mm comprising the mixture was formed. While, an aluminum foil on a periphery of which denatured polypropylene forming the sealing material was installed, was prepared. The foregoing composite sheet was press bonded onto the aluminum foil to prepare the cathode.

On the other hand, 95 weight parts carbon powder forming the negative active material and 5 weight parts of polytetrafluoroethylene forming the binder were mixed, so that a composite sheet having a thickness of 0.2 mm comprising the mixture was formed. The composite sheet was press bonded onto a nickel foil to form the anode. An electrolyte comprising ethylene carbonate solution dissolved with LiPF_6 of 1 mol. was impregnated under reduced pressure to a separator comprising polypropylene porous film, the cathode and the anode.

The cathode, the separator and the anode were laminated, and the peripheral sealing material was heat sealed to complete the battery.

(Comparison example 9)

In a battery of this comparison example; the amount of acetylene black in the composite sheet of cathode was 10 weight parts, the palladium treated carbon was omitted, and the other components were same with those of the embodiment 16.

(Embodiment 17)

In a battery of this embodiment; the composite sheet of anode was formed by mixing 92 weight parts of carbon powder, 25 weight parts of polytetrafluoroethylene and 3 weight parts of palladium treated carbon same with that of the embodiment 1, and the other components were same with those of the comparison example 9.

(Test 10)

Charge/discharge cycle tests were done on the batteries of embodiments 16 and 17 and comparison example 9, to examine respective charge/discharge cycle characteristics at initial stage and after long-term preservation. An electrode surface area could be changed variously depending on manufacturing process, however, it was set to 100 cm² in these tests.

Conditions of charge/discharge cycle tests were a temperature of 25 °C, a constant current per unit area of 0.5 mA/cm², a charge end voltage of 4.1V, and a discharge end voltage of 2.7V.

A period of long-term preservation was 100 days at 60 °C.

Fig. 12 shows charge/discharge cycle characteristics at initial stage and after long-term preservation. In the figure, X16(i) and X17(i) denote charge/discharge cycle characteristics at initial stage of the batteries of embodiments 16 and 17, X16(p) and X17(p) denote charge/discharge cycle characteristics after long-term preservation of the batteries of embodiments 16 and 17 respectively, Y9(i) denotes a charge/discharge cycle characteristic at initial stage of the battery of comparison example 9, and Y9(p) denotes a charge/discharge cycle characteristic after long-term preservation of the battery of comparison example 9. Further, an axis of abscissa represents a charge/discharge cycle number (time) and an axis of ordinate represents a battery capacity (mAh).

As obvious from Fig. 12, capacity decreases at initial stage accompanied by elapse of cycle were small and capacity decreases after long-term preservation were also small in the batteries of embodiments 16 and 17. However, the both capacity decreases were large in the battery of comparison example 9. Further, no expansion was produced in the batteries of embodiments 16 and 17 during the tests. However, the expansion was produced in the battery of comparison example 9 as the cycle advanced and the expansion was positively produced after long-term preservation. It can be considered that, in the battery of comparison example 9, an impedance of battery inside was increased by the expansion to cause the decrease in capacity.

In the foregoing embodiments, the palladium treated carbon etc. included in the electrode composites may be used by being previously smeared to the active material.

Industrial Applicability

The battery of this invention, which is provided with a high long-term reliability and controlled its expansion and bursting, has a large industrial value in use.

Claims

1. A battery equipped, in an inside surrounded by a current collector and a sealing material, with a cathode composite including an active material and a material other than it, an anode composite including an active material and a material other than it or an anode comprising the active material only, and an electrolyte, in which an ion-conductive high-molecular compound including one or more kinds of ionic compound in a dissolved state is used as a composition material, for at least one of the cathode composite, the anode composite and the electrolyte; characterized by that one or more kinds of materials having such property that gas produced in a battery inside is absorbed by the material itself or added to residual reactive double bond in the ion-conductive high-molecular compound, are included in the battery inside.

2. A battery as set forth in claim 1, in which said material exists in or on a surface of the cathode composite.
3. A battery as set forth in claim 1, in which said material exists in or on a surface of the anode composite.
4. A battery as set forth in claim 1, in which said material exists on a surface of the anode.
5. A battery as set forth in claim 1, in which said material exists on a surface of the sealing material.
6. A battery as set forth in claim 1, in which said material exists in the electrolyte layer.
7. A battery as set forth in claim 1, in which said material is an element belonging to VIII-group of periodic table.
8. A battery as set forth in claim 7, in which said element is palladium, ruthenium, rhodium or platinum.
9. A battery as set forth in claim 1, in which said material is palladium treated carbon, palladium treated MnO_2 , platinum black, platinum treated carbon, misch metal alloy or LaNi_5 .
10. A battery as set forth in claim 9, in which the misch metal is $\text{MmNi}_{3.7}\text{Fe}_{0.3}\text{Al}_{0.3}\text{Co}_{0.7}$.
11. A battery as set forth in claim 1, in which said material is active carbon zeolite, hollow glass fine sphere, ethyl ether, acetone, gelatin, starch or dextrin.
12. A battery as set forth in claim 1, in which at least one of the cathode composite and the anode composite includes a binder.
13. A battery as set forth in claim 1, in which the ion-conductive high-molecular compound is formed by polymerization reaction created by irradiation of ionizing radiation or ultraviolet ray.
14. A battery as set forth in claim 1, in which the ion-conductive high-molecular compound is formed by polymerizing a high-molecular compound, which has a reactive double bond and polyether bond, so as to include a crosslink network structure.
15. A battery as set forth in claim 1, in which the ion-conductive high-molecular compound includes an organic compound which can dissolve an ionic compound.
16. A battery as set forth in claim 1, in which the anode composite includes a carbon material as an active material.

Fig. 1

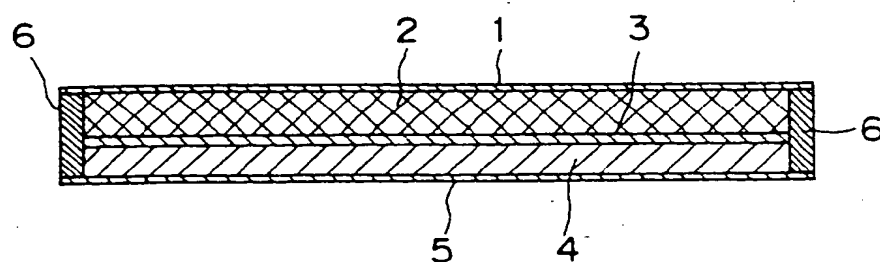


Fig. 2

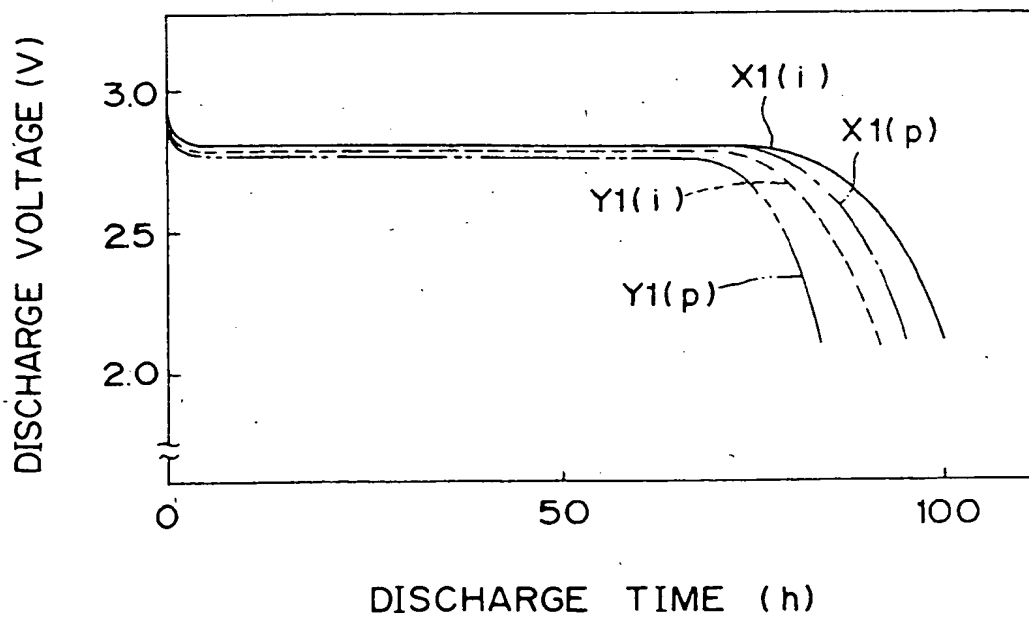


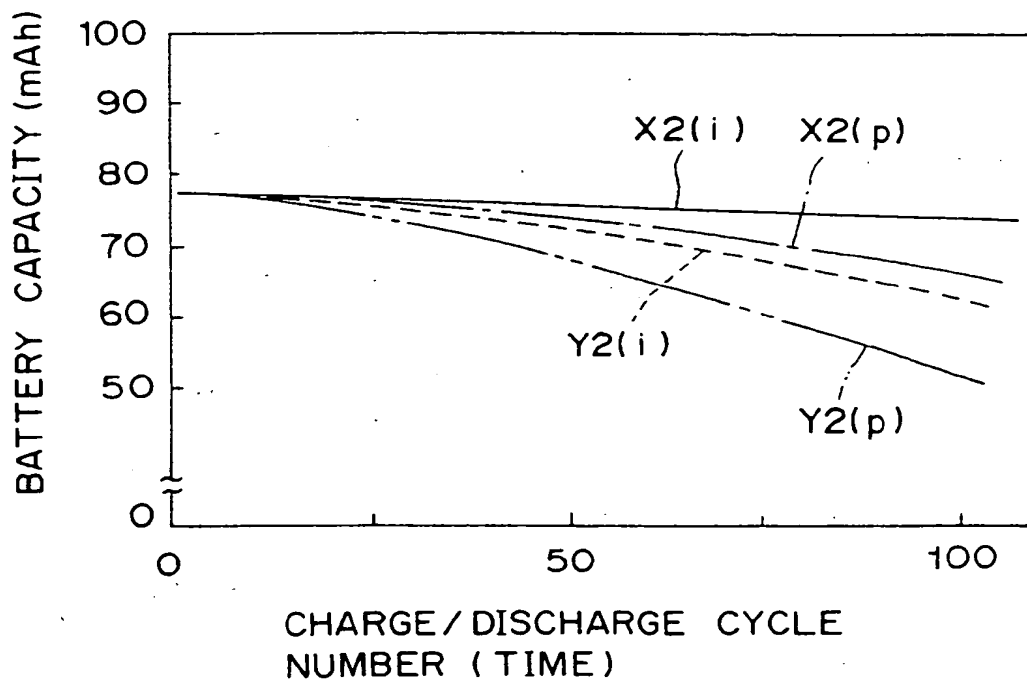
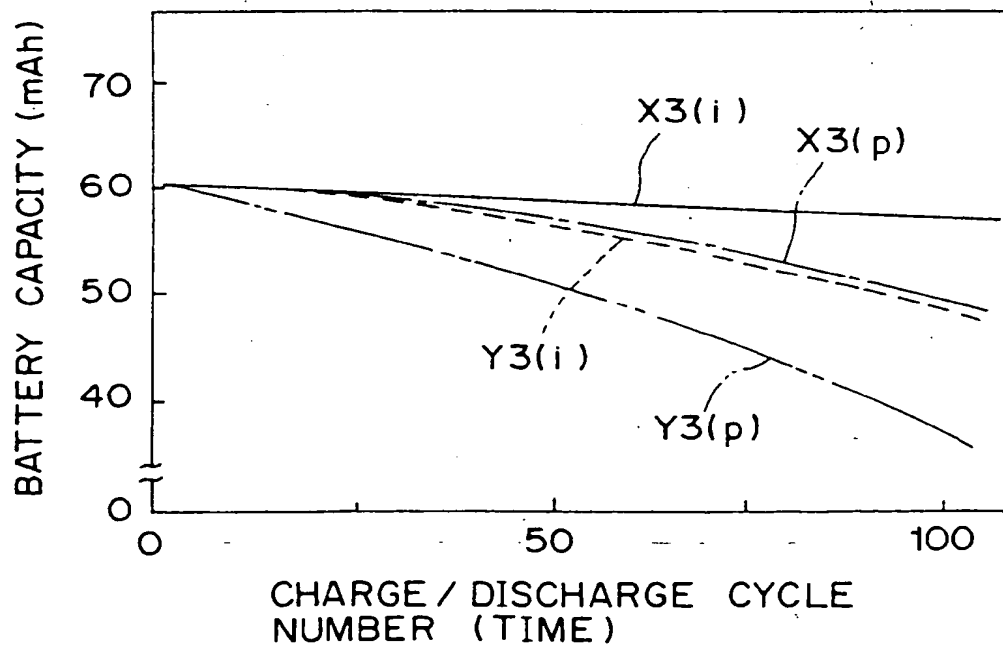
Fig. 3*Fig. 4*

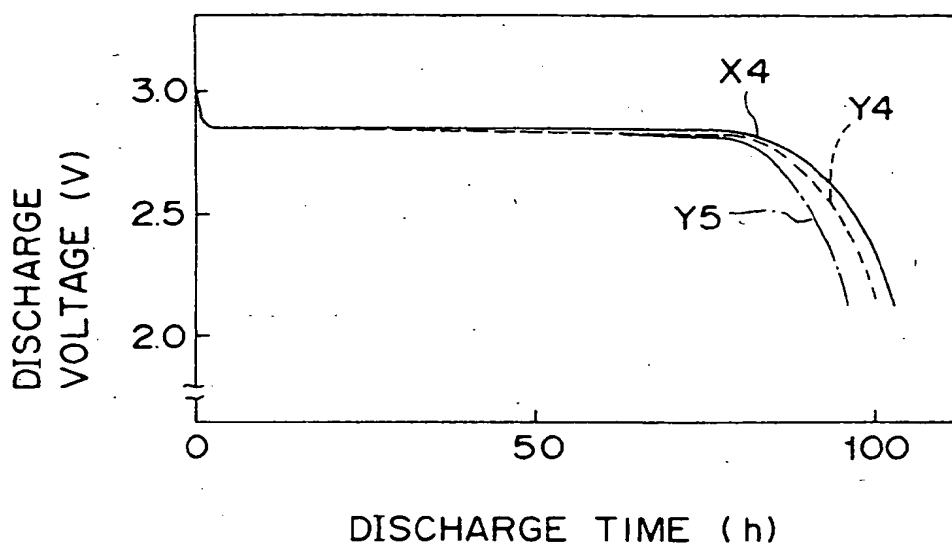
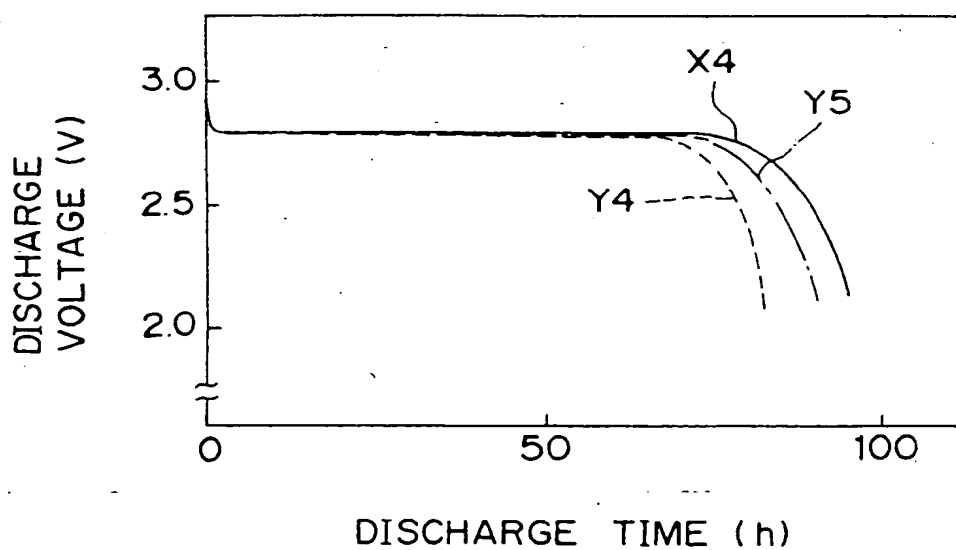
Fig. 5*Fig. 6*

Fig. 7

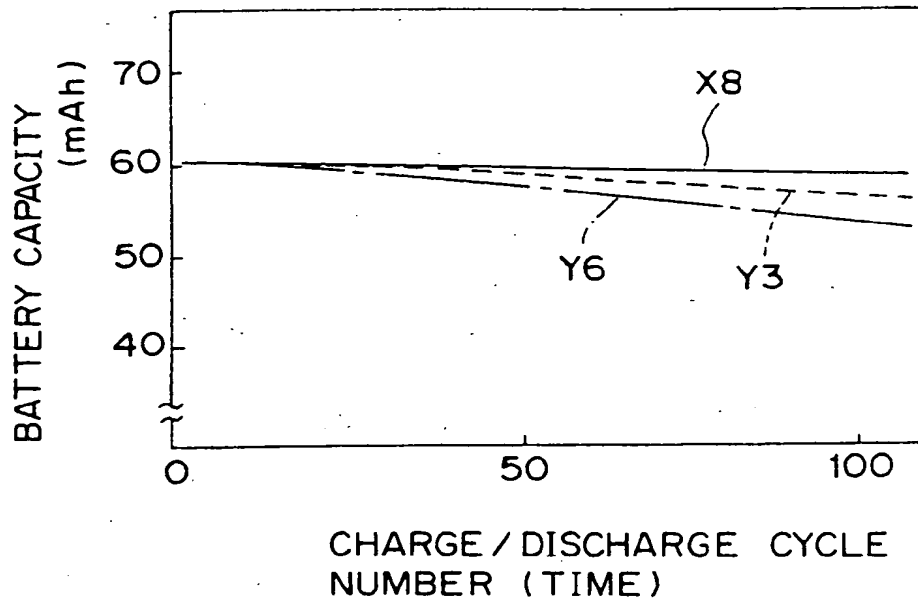


Fig. 8

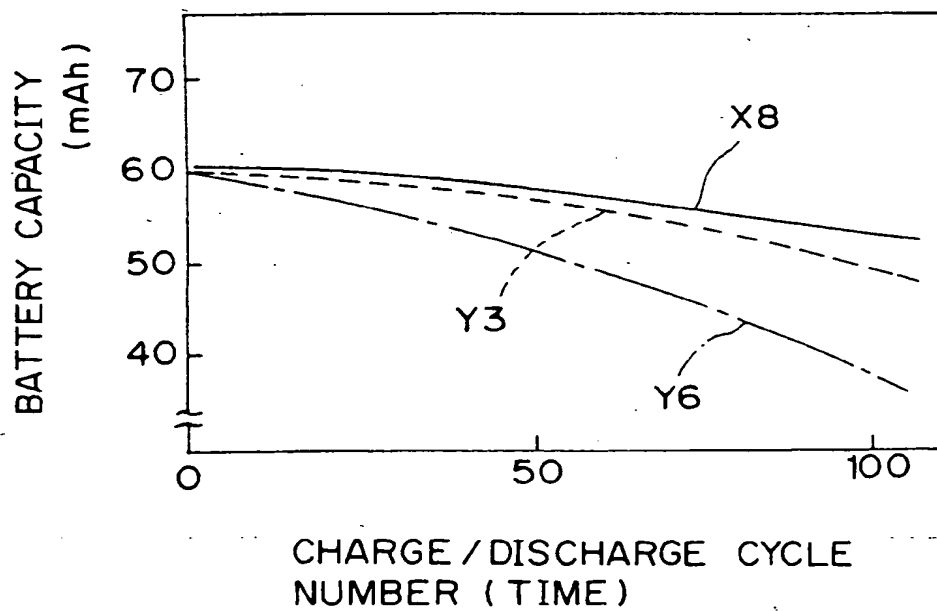


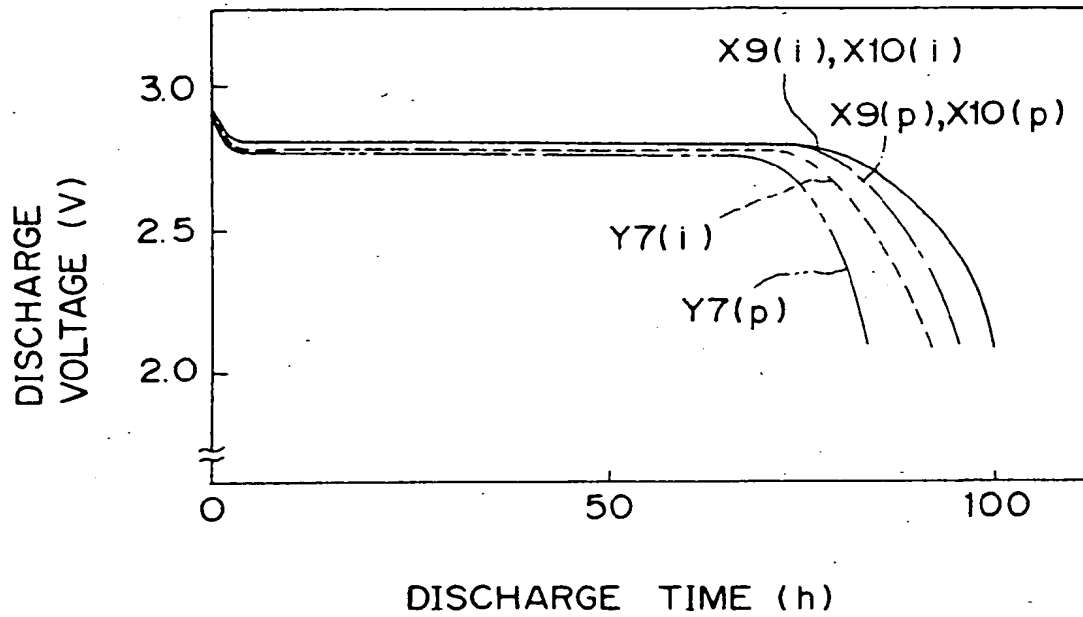
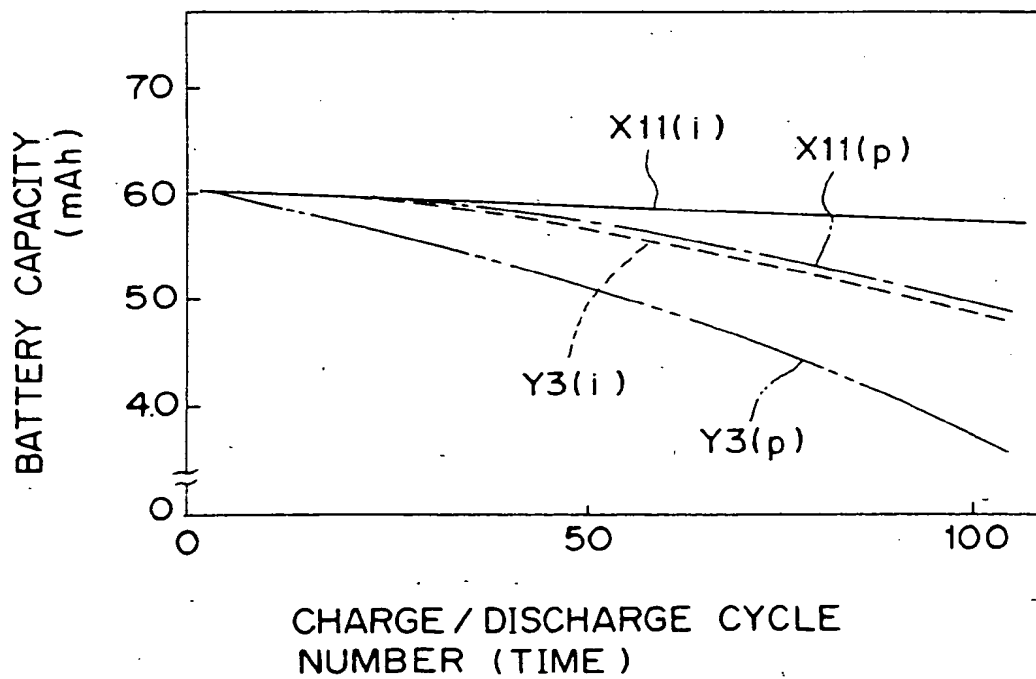
Fig. 9*Fig. 10*

Fig. 11

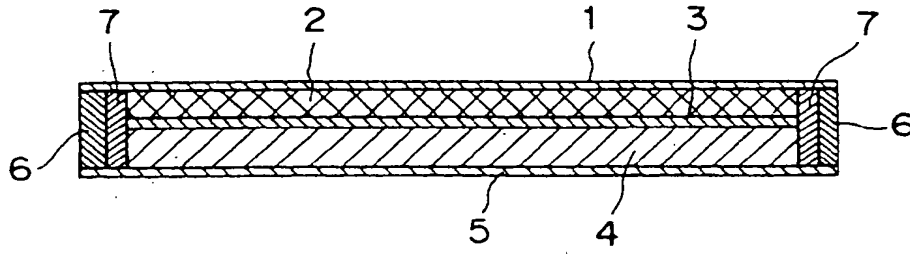
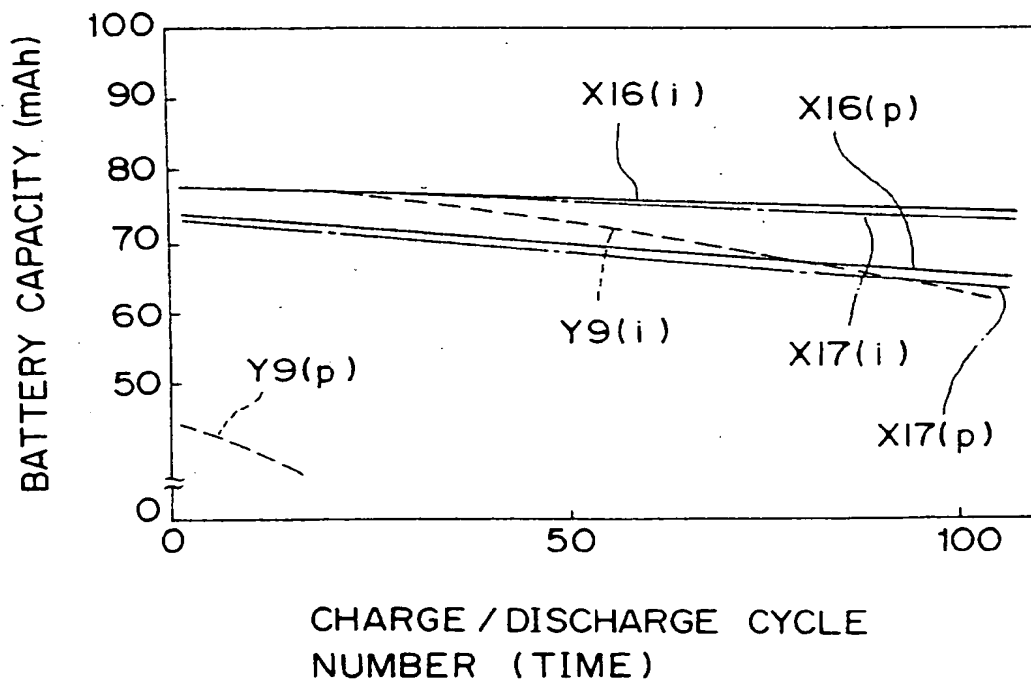


Fig. 12



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP93/00880

A. CLASSIFICATION OF SUBJECT MATTER		
Int. Cl ⁵ H01M10/52		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols)		
Int. Cl ⁵ H01M10/52, 10/40		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Jitsuyo Shinan Koho 1926 - 1993		
Kokai Jitsuyo Shinan Koho 1971 - 1993		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, A, 60-127669 (Asahi Chemical Industry Co., Ltd.), July 8, 1985 (08. 07. 85), (Family: none)	1
A	JP, B2, 53-34295 (The Furukawa Battery Co., Ltd.), September 20, 1978 (20. 09. 78), (Family: none)	2-12
A	JP, A, 48-69784 (Yuasa Battery Co., Ltd.), September 21, 1973 (21. 09. 73), (Family: none)	2-12
A	JP, B2, 56-32740 (Hitachi Maxell, Ltd.), July 29, 1981 (29. 07. 81), (Family: none)	2-12
A	JP, A, 1-107470 (Hitachi Maxell, Ltd.), April 25, 1989 (25. 04. 89), (Family: none)	13-15
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search		Date of mailing of the international search report
September 14, 1993 (14. 09. 93)		September 28, 1993 (28. 09. 93)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP93/00880

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, A, 1-109665 (Minolta Camera Co., Ltd.), April 26, 1989 (26. 04. 89), & US, A, 4906537	13
A	JP, A, 63-301469 (The Dow Chemical Co.), December 8, 1988 (08. 12. 88), & US, A, 4728588 & EP, A2, 293946	16

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

Fig. 1

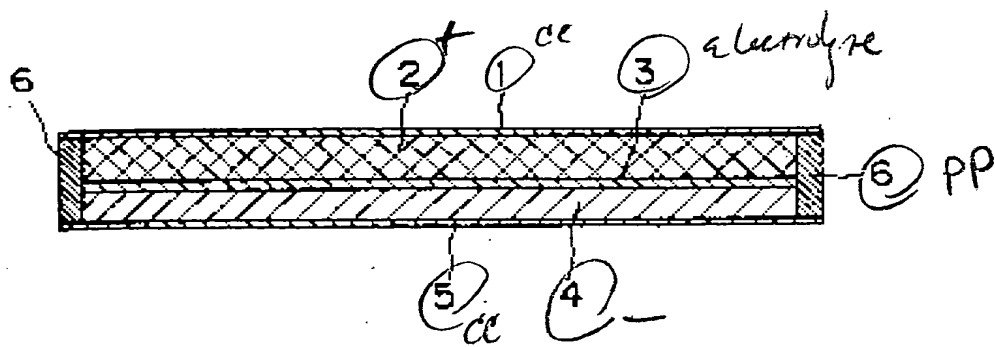


Fig. 2

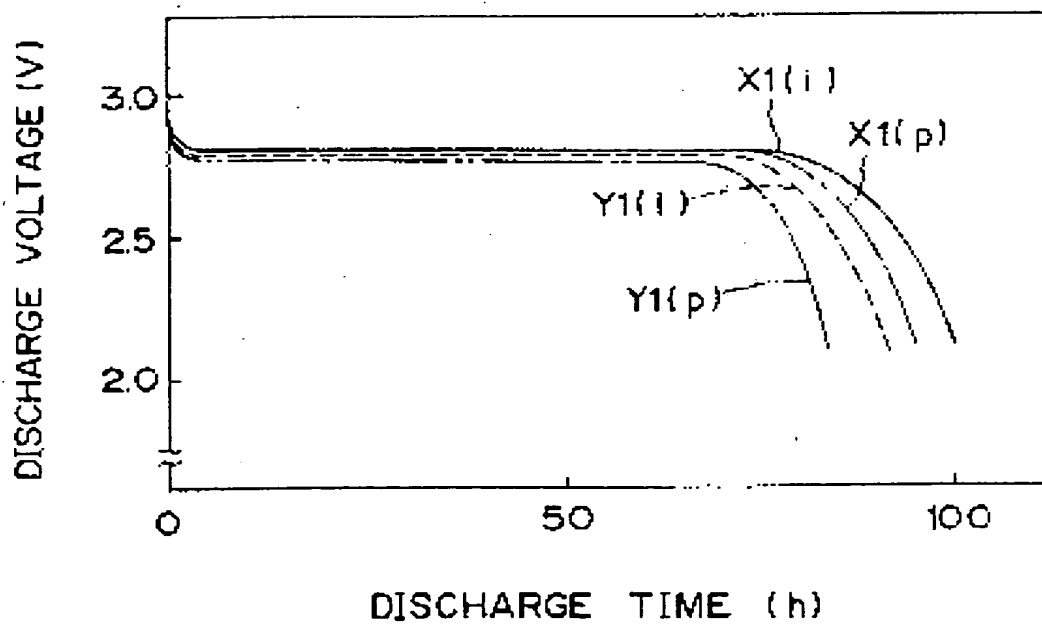


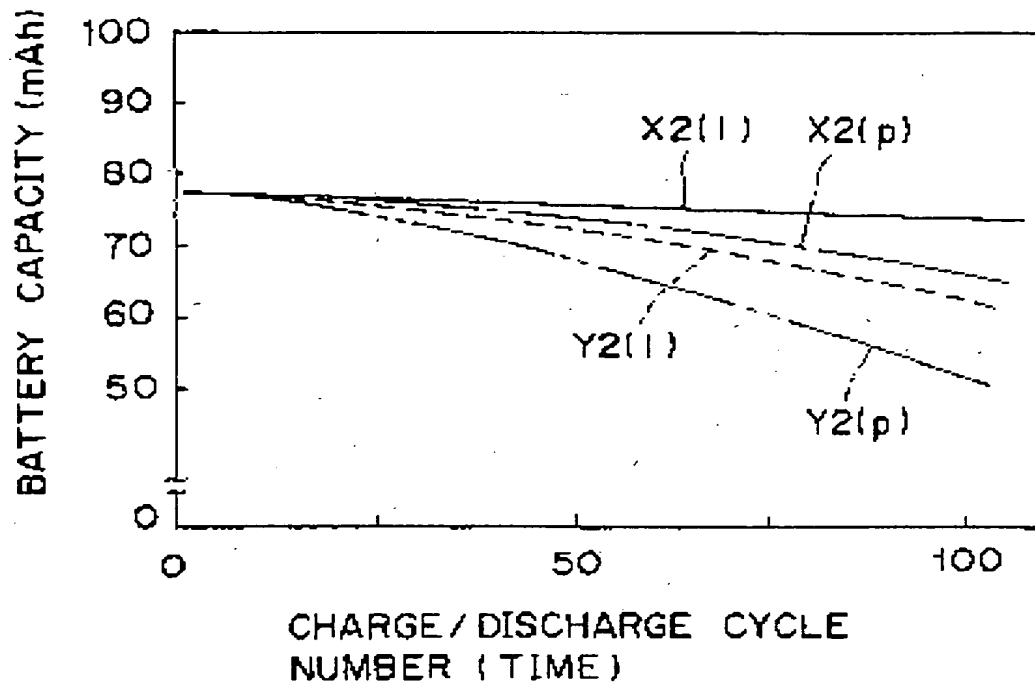
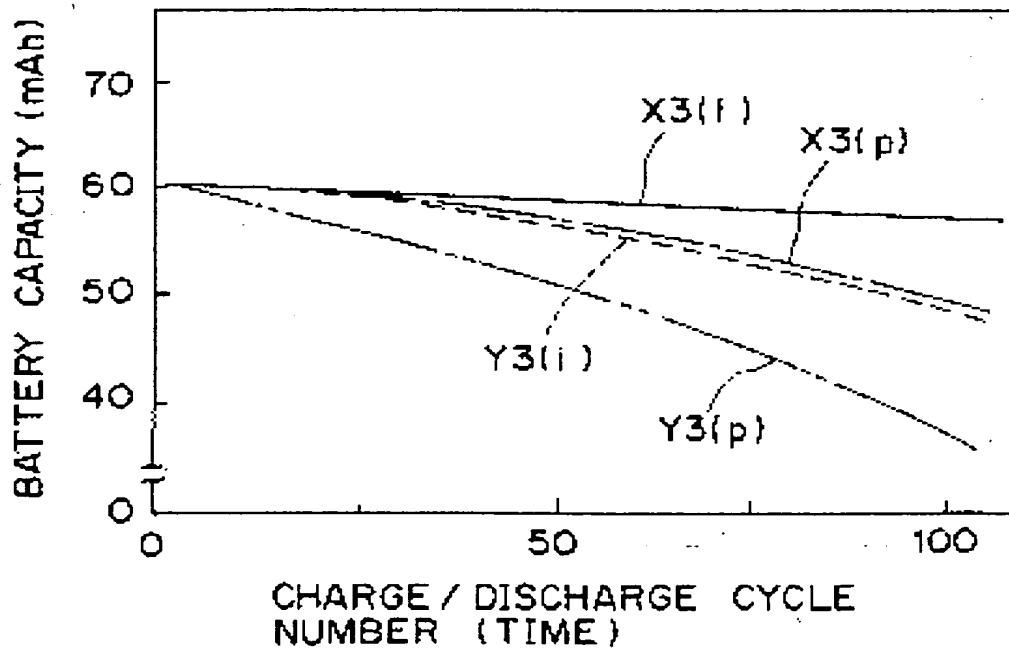
Fig. 3*Fig. 4*

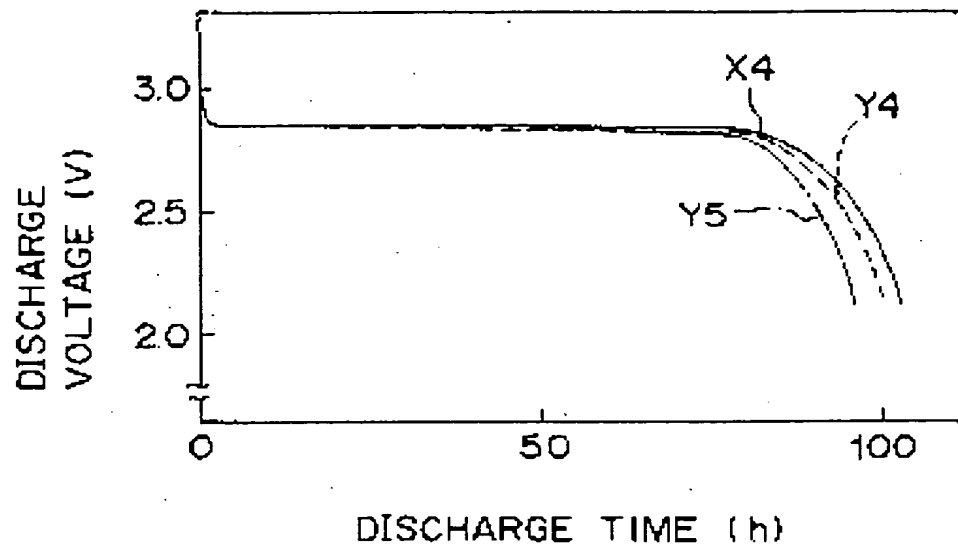
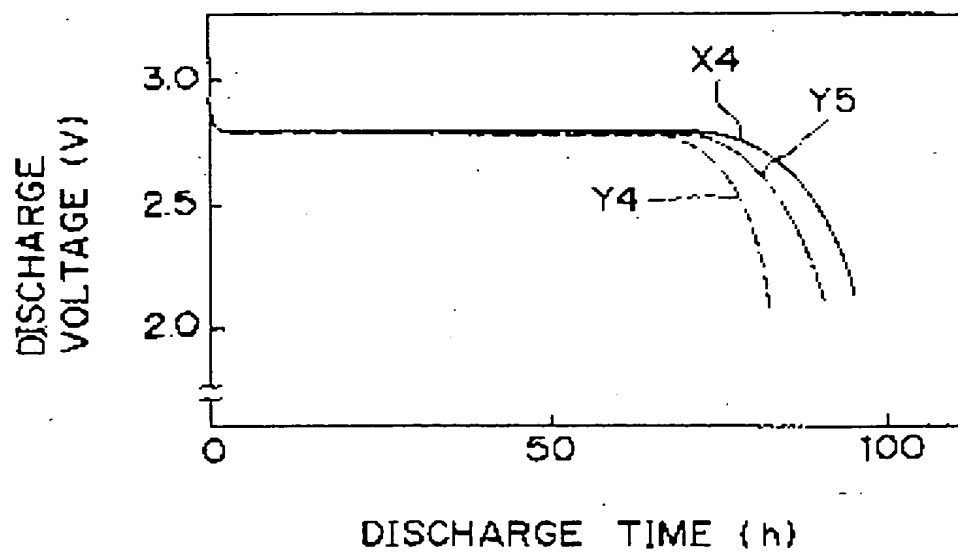
Fig. 5*Fig. 6*

Fig. 7

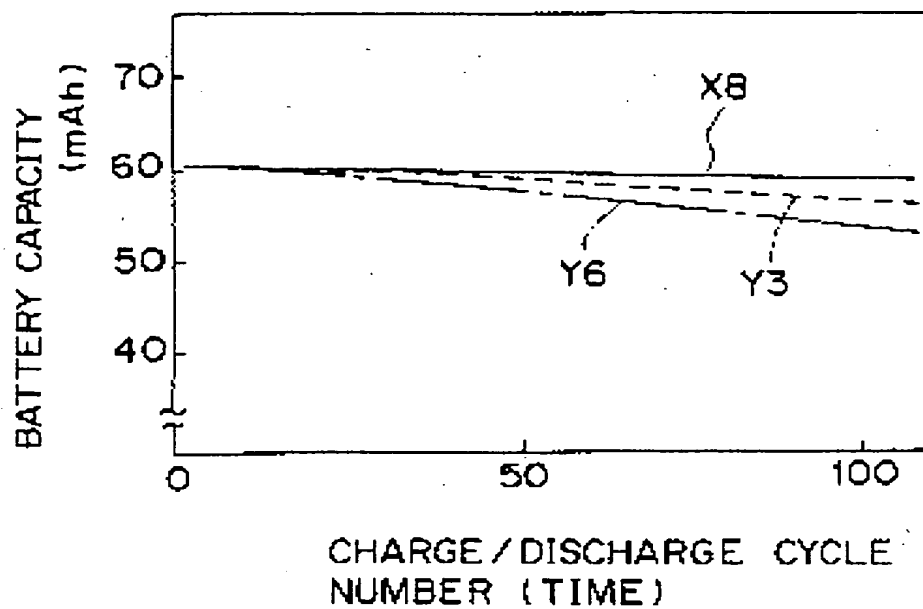


Fig. 8

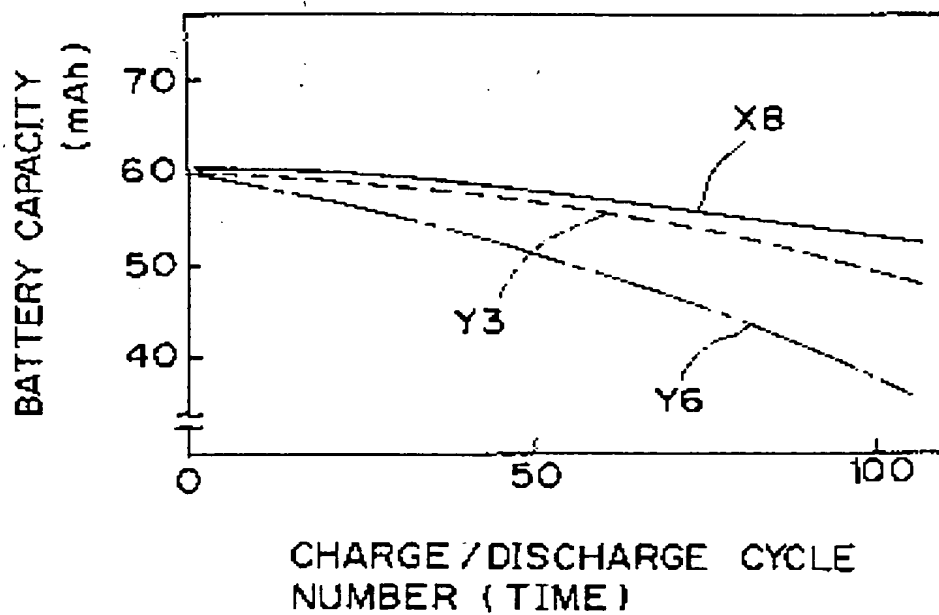


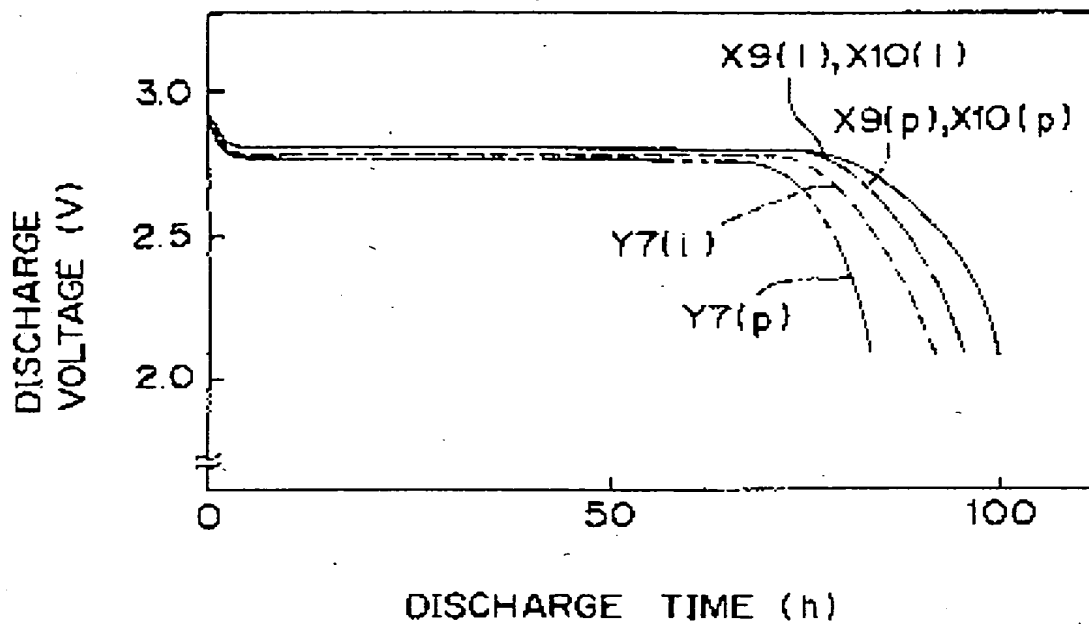
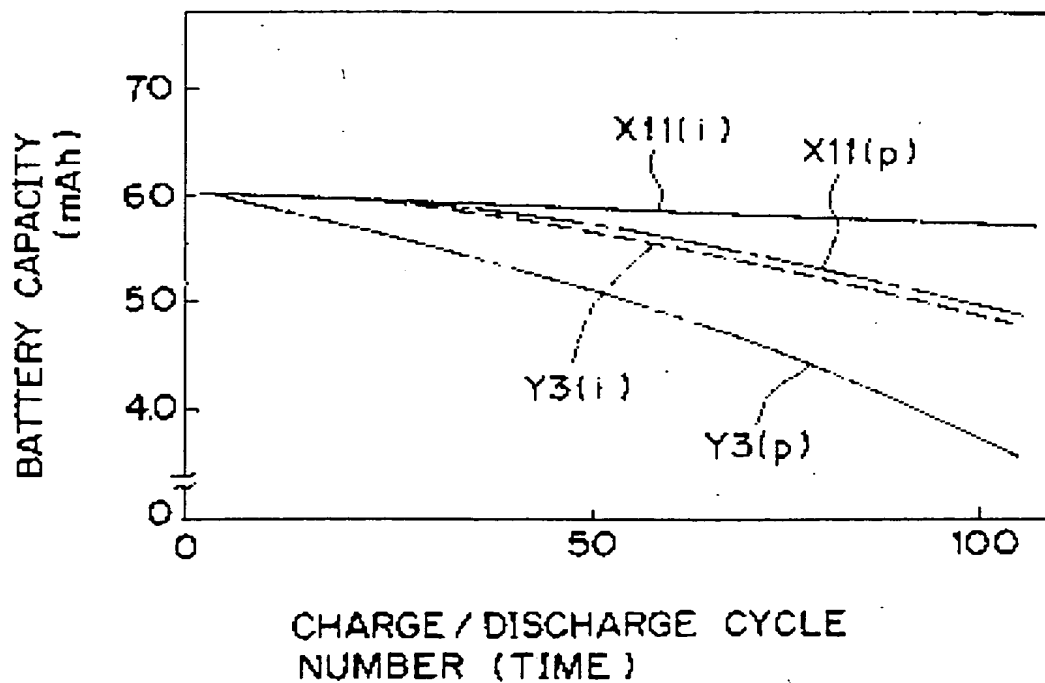
Fig. 9*Fig. 10*

Fig. 11

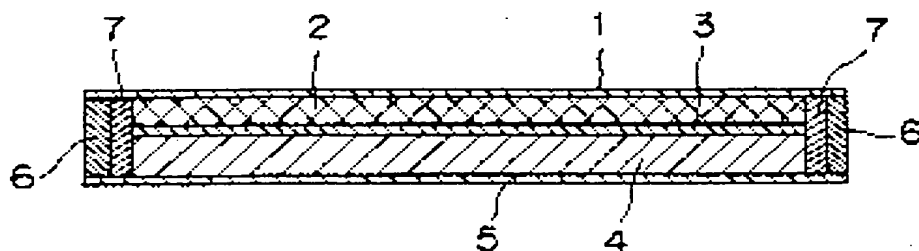


Fig. 12

